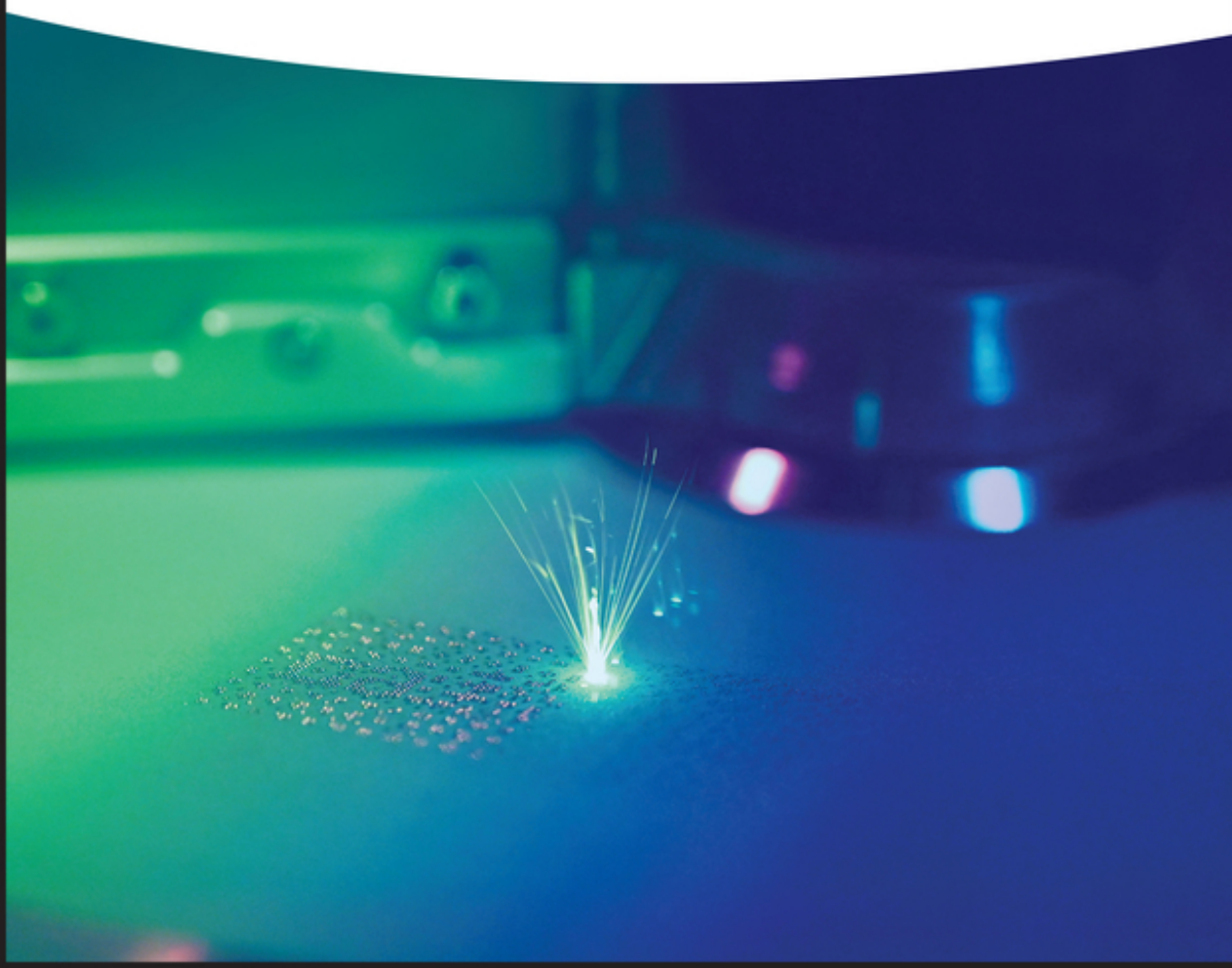


Kun Zhou and Changjun Han

Metal Powder-Based Additive Manufacturing



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Biography

Kun Zhou is a Professor of Mechanical Engineering in the School of Mechanical and Aerospace Engineering at Nanyang Technological University, Singapore. His research interests focus on mechanics of materials and additive manufacturing. He has founded the journal *Smart Manufacturing* and serves as its Editor-in-Chief. He is also a co-founder of *Journal of Micromechanics and Molecular Physics* and serves as its Co-Editor-in-Chief. He was elected Fellow of Institution of Mechanical Engineers, Royal Aeronautical Society, Royal Society of Chemistry, Institute of Physics, and Institute of Materials, Minerals & Mining.

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Preface

Additive manufacturing (AM), commonly known as three-dimensional (3D) printing, has emerged as a revolutionary technology capable of fabricating parts with complex geometries in a layer-by-layer manner, thereby granting unprecedented design freedom. It has evolved from a tool primarily employed for rapid prototyping into a well-recognized technology for producing functional parts with highly desirable properties. This technology provides a cost-effective option for the low-volume production of highly specialized parts for a wide variety of applications in the aerospace, art, biomedical, automotive, electronics, manufacturing, energy, building and construction, marine, “oil and gas industries”.

Powder-based AM is a major subset of the AM family, in which parts are using powders as feedstock materials. Within this category, powder bed fusion (PBF), directed energy deposition (DED), and binder jetting are presently the predominant techniques. In particular, laser powder bed fusion (LPBF), electron beam melting (EBM), laser-based directed energy deposition (L-DED), and metal binder jetting (MBJ) are commonly adopted powder-based AM processes for printing metal parts.

The production of defect-free and structurally sound parts through metal powder-based AM requires an in-depth understanding of the feedstock materials, the printing processes, and the underlying mechanisms of defect formation in the printed parts. Notably, metal powder-based AM is multidisciplinary in nature and entails key concepts from different subjects, including materials science, engineering, powder metallurgy, physics, and chemistry. Therefore, understanding the fundamentals of metal powder-based AM may constitute a daunting challenge for novice researchers.

This book introduces the fundamentals of powder preparation processes and metal powder-based AM techniques while emphasizing their significance in various industrial applications. For more experienced AM practitioners, the recent progress of metal powder-based AM techniques is reviewed along with noteworthy case studies, which feature the wide applicability of metal powder-based AM techniques.

Chapter 1 presents a brief introduction to metal powder-based AM. The history and fundamentals of AM are first highlighted, followed by seven categories of AM techniques with their representative processes and commercial companies. Next, different types of post-processing treatment techniques for metal AM parts

are illustrated. Powder properties and characterization methods are also discussed comprehensively. Finally, the challenges and future trends of metal powder-based AM are outlined. Researchers who are unfamiliar with metal powder-based AM techniques are encouraged to peruse this chapter to attain a solid understanding of these principles.

Chapter 2 presents the fundamentals of the preparation processes of metal powders for AM, specifically, atomization, mechanical mixing, the reduction process, and powder modification. A comprehensive review of the relationships between the preparation processes and powder properties is provided. For more experienced researchers, this chapter serves as a concise handbook in which the key concepts underlying AM powder metallurgy are succinctly explained.

Chapters 3–6 delve into various metal powder-based AM techniques, namely, LPBF, EBM, L-DED, and MBJ. Chapter 3 focuses on the LPBF technique, with regard to its history, fundamentals, printing process, metallurgical defects, powder materials, equipment, and the microstructures and mechanical properties of the representative materials investigated for the printed parts. In particular, the characteristics of popular LPBF-printed mechanical metamaterials, which typically correspond to a high Young's modulus, high shear and bulk moduli, and zero or negative Poisson's ratio, are comprehensively evaluated.

In Chapter 4, the EBM technique is introduced with an overview of its history, fundamentals, processing characteristics, powder materials, equipment, and the microstructures and mechanical properties of the most extensively studied materials for the printed parts. The preheating and melting processes during EBM printing are also described, and their influence on the surface quality of the printed parts is discussed.

Chapter 5 expounds on the L-DED technique in terms of its history, fundamentals, deposition process, metallurgical defects, powder materials, equipment, and the microstructures and mechanical properties of the representative materials for the printed parts. Additionally, the unique capability of L-DED to fabricate multi-materials and functionally graded materials is highlighted.

Chapter 6 is devoted to the MBJ technique, with respect to its history, fundamentals, printing process, powder and binder materials, equipment, and the microstructures and mechanical properties of the representative materials for the printed parts. The unique ability of MBJ to print parts using refractory metals, magnesium and its alloys, and magnetic alloys, which are difficult to print using the abovementioned three techniques, is also examined.

Chapter 7 reports on the latest advances in metal powder-based AM products in the aerospace, biomedical, automotive, molding and tooling, energy, marine, oil and gas, and jewelry industries. This chapter focuses on providing insights of both academic and industrial relevance to readers and keeping them abreast of recent applications involving metal AM.

The completion of this book could not have been possible without the excellent teamwork displayed by the members of our research group, with whom our discussions have always been fruitful. We greatly appreciate the efforts of Liming You, Chengcheng Wang, Haiyang Fan, Yujia Tian, Jiazhao Huang, Boyuan Li, Zhuohong

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Singapore, December 2022

Kun Zhou
Changjun Han

1

Introduction

This chapter presents a brief introduction to metal powder-based additive manufacturing (AM). The history and fundamentals of AM are first highlighted. Seven categories of AM techniques with their representative processes and commercial companies are then presented, followed by an overview of the types of metal powder-based AM techniques. Next, the types of post-processing treatments for metal AM parts are illustrated. Powder properties and characterization methods are also discussed comprehensively. Finally, the challenges and future trends of metal powder-based AM are outlined.

1.1 History and Fundamentals of AM

Additive manufacturing (AM), commonly known as three-dimensional (3D) printing, has emerged as a revolutionary technology capable of fabricating parts with complex geometries in a layer-by-layer manner, thereby granting extensive freedom of design (Martin et al. 2017; Kelly et al. 2019; Zhang et al. 2019). The term “additive manufacturing” describes “the process of joining materials to make parts from 3D model data, usually layer upon layer, as opposed to subtractive manufacturing and formative manufacturing methodologies”, according to the ISO/ASTM 52900 standard (ISO and ASTM International 2015). ISO and ASTM are the abbreviations for the International Standards Organization and the American Society for Testing and Materials, respectively. The most commonly used term before AM was “rapid prototyping”, which is currently considered outdated because of the increasingly extensive applications of the process.

The advent of AM marks an important milestone in the history of manufacturing. In 1987, Stereolithography Apparatus-1, the first commercial AM system, was launched by 3D Systems in the United States. The system enabled the printing of 3D parts from a computer-aided design (CAD) model for the first time. Other AM techniques were introduced for commercial purposes soon thereafter, which include fused deposition modeling, selective deposition lamination, selective laser sintering, and laminated object manufacturing. Machines operating based on the inkjet printing process began appearing on the market in 1996. In 1998, Optomec delivered the first laser engineered net shaping metal powder system capable of producing

near-fully dense metal parts. Meanwhile, in 1999, a selective laser melting system was initiated by Fockele & Schwarze of Germany.

The expiry of old AM patents, such as the fused deposition modeling technique (which expired in 2009), has led to a surge in the number of low-cost personal AM machines on the consumer market, some of which can even be assembled by hand. Moreover, the rise of online platforms, such as open-source communities where AM design files are shared freely, further improves the accessibility of 3D printing technology. In 2014, the number of AM patents that expired has reached a peak, which has led to a greater variety of low-cost machines flooding the consumer market.

Over the years, AM has evolved from a tool primarily used for visualization (i.e. rapid prototyping) into a well-recognized technology for producing functional parts with desirable properties. Before printing, a 3D model is constructed via CAD and mathematically sliced into ultrathin printed layers along the build direction. Subsequently, the layers are printed according to their predefined shapes, with consecutive layers bonding to each other.

AM also provides a cost-effective option for low-volume customized production, which differs from conventional mold jetting methods. Parts comprising multiple components can be redesigned as single units and fabricated efficiently without assembly (Chua and Leong 2017). The distinct ability of this process to manufacture complex shapes and structures has already rendered it invaluable for producing prototypes or parts in industries including aerospace, military, biomedical, automotive, electronics, energy, molding, building and construction, marine and offshore, education, art, robotics, environment, and social culture.

AM is also perceived as an environmentally sustainable manufacturing technology, as it can potentially reduce up to 525.5 Mt of total carbon dioxide emissions by 2025 compared to conventional processes (Gebler et al. 2014; Ribeiro et al. 2020). Furthermore, in terms of product development, AM can reduce up to 70% of development costs and time-to-market by up to 90% compared to conventional processes (Gibson et al. 2014). With such remarkable benefits, the global market for AM is projected to reach nearly US\$23 billion by 2023, with a compound annual growth rate of 22% (Tan et al. 2020).

1.2 AM Techniques

AM technologies have been classified into seven broad categories according to the ISO/ASTM 52900 standard, namely, vat photopolymerization, material jetting, material extrusion, powder bed fusion (PBF), directed energy deposition (DED), binder jetting, and sheet lamination techniques (ISO and ASTM International 2015), as shown in Figure 1.1. Table 1.1 provides an overview of the representative processes and commercial companies of these AM categories.

The vat photopolymerization technique utilizes radiation (e.g. ultraviolet [UV] and visible light) to selectively polymerize liquid photosensitive resins in a vat to form high-resolution solid 3D structures. It includes various processes such as stereolithography (Hull 1986), digital light processing (Kuang et al. 2019), continuous liquid interface production (Tumbleston et al. 2015), two-photon photopolymerization

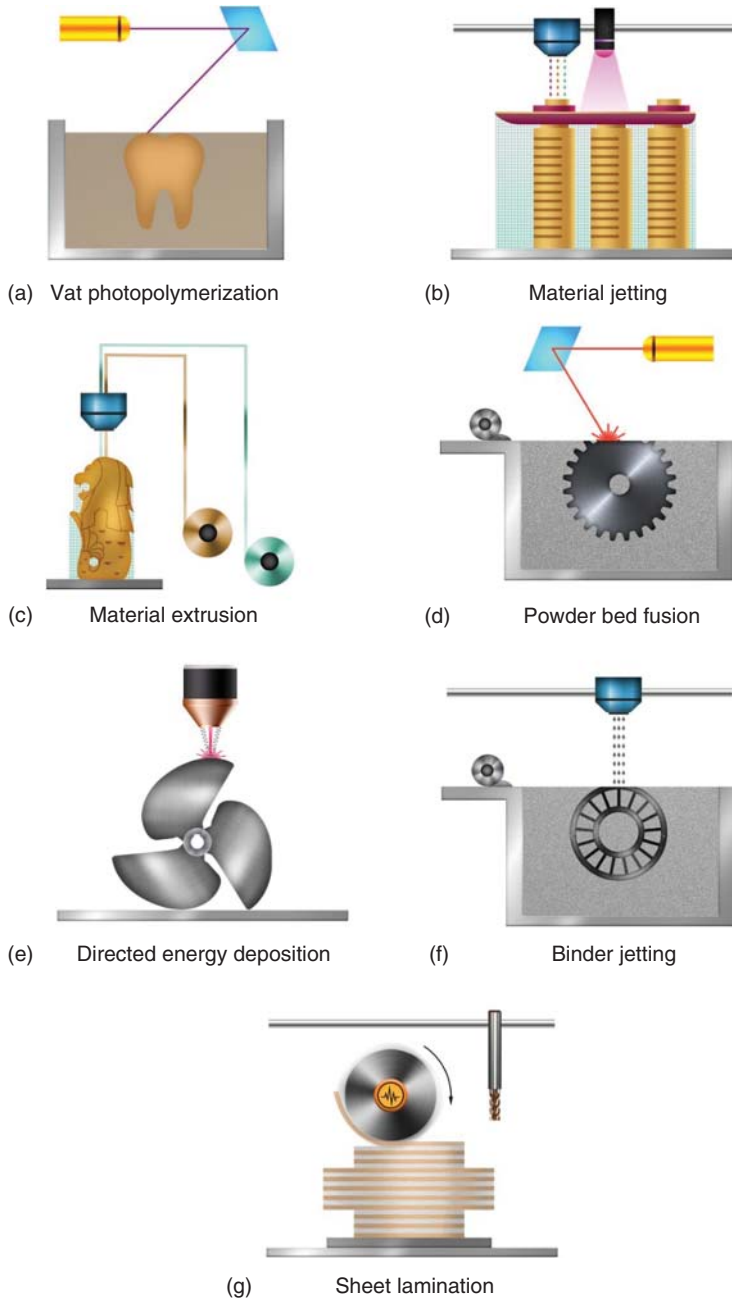


Figure 1.1 Schematics of the seven broad categories of AM technologies according to the ISO/ASTM 52900 standard. Source: ISO and ASTM International (2015)/ISO.

Table 1.1 AM categories, and their representative processes and commercial companies.

AM categories	Representative AM processes	Representative commercial companies	
Vat photopolymerization	Stereolithography	USA	3D Systems, Stratasys, Carbon, Formlabs
	Digital light processing		
	Continuous liquid interphase production	Germany	Envisiontec
	Computed axial lithography	China	UnionTech, ZRapid
	Two-photon photopolymerization	France	Prodways
	High-area rapid printing	Australia	Lithoz
		Netherlands	Admatec
		Italy	Sisma, DWS
		Denmark	AddiFab
Material jetting	PolyJet	USA	3D Systems, Stratasys, Optomec, Solidscape, nScrypt
	MultiJet		
	Aerosol jet		
	NanoParticle jetting	Israel	Xjet, Nano Dimension
Material extrusion	Electrohydrodynamic jetting	Japan	Mimaki
	Fused deposition modeling (Fused filament fabrication)	USA	Stratasys, Markforged, Essentium, Robocasting, Cincinnati
	Direct ink writing		
	3D dispensing	Germany	Arburg, BigRep
	(3D plotting)	Netherlands	Ultimaker
Powder bed fusion	Laser powder bed fusion (Selective laser melting)	USA	3D Systems, HP Inc., GE Additive, Velo3D
	(Direct metal laser sintering)	Germany	SLM Solutions, EOS, Trumpf, Voxeljet
	Electron beam melting		
	Selective laser sintering	China	Bright Laser Technologies, Farsoon Technologies, Eplus 3D, Laseradd
	Multi jet fusion		
	High speed sintering	UK	Renishaw
		Italy	Sisma
Directed energy deposition	Laser-based directed energy deposition (Laser engineered net shaping)	USA	Optomec, Sciaky, Addere, Formally
	(Laser metal deposition)	Germany	Trumpf, DMG Mori
	Laser wire additive manufacturing	China	Bright Laser Technologies
	Wire arc additive manufacturing	France	BeAM
		Australia	AML3D
	Electron beam freeform fabrication (Electron beam additive manufacturing)	Netherlands	MX3D
		Japan	Sodick
		South Korea	InssTek
		Spain	Addilan

Table 1.1 (Continued)

AM categories	Representative AM processes	Representative commercial companies	
Binder jetting	Binder jetting	USA	3D Systems, HP Inc., Exone, Desktop Metal, Digital Metal
		Germany	Voxeljet
		China	Long Yuan
		UK	Raplas
		USA	Fabrisonic, Evolve Additive, Impossible Objects
Sheet lamination	Laminated object manufacturing Ultrasonic additive manufacturing Selective deposition lamination Composite-based additive manufacturing		

(Saha et al. 2019), high-area rapid printing (Walker et al. 2019), and computed axial lithography (Kelly et al. 2019). Representative companies for vat photopolymerization include 3D Systems (USA), Carbon (USA), Envisiontec (Germany), Lithoz (Australia), and UnionTech (China).

Figure 1.1a illustrates the top-down stereolithography process, a typical vat photopolymerization technique. Stereolithography is a common vat photopolymerization technique that utilizes an UV laser source positioned above or underneath a resin vat to selectively cure the exposed layer.

The material jetting technique is analogous to traditional two-dimensional (2D) inkjet printing, in which liquid materials (e.g. photosensitive resins, thermoplastics, wax, and reactive materials) are deposited from inkjet printheads onto a build platform through either a drop-on-demand or a continuous approach and subsequently solidified through photopolymerization, cooling, etc. This technique is employed in commercialized systems such as PolyJet, MultiJet, Aerosol Jet, and NanoParticle Jet, as well as non-commercialized systems based on electrohydrodynamic jetting.

Figure 1.1b shows a schematic of the material jetting technique. For example, in the PolyJet system, multiple depositions of photosensitive build materials and support materials (to form the support structures within the printed parts) in the form of droplets are made by nozzles in the printhead before undergoing UV curing. During post-processing, the support structures are removed through mechanical (cutting with a water jet system) and/or chemical (dissolving with a solvent) procedures. Representative companies of material jetting include Stratasys (USA), 3D Systems (USA), Optomec (USA), Xjet (Israel), and Nano Dimension (Israel).

The material extrusion technique typically involves a continuous extrusion of polymer filaments, viscous inks, or even polymer pellets through a heated nozzle onto a build platform, on which the extruded molten material subsequently

solidifies. Fused deposition modeling (also known as fused filament fabrication) and direct ink writing are the key representative processes in this category. The former utilizes thermoplastic filaments and pellets as feedstock materials, while the latter employs viscous inks such as pastes and concentrated polymer solutions (Truby and Lewis 2016). Recent studies have also established the significant potential of fused deposition modeling in printing metal parts. For example, in one such study, printable filaments were prepared through the extrusion of a polyolefin-based binder mixed with 59 vol.% Ti-6Al-4 V powder and then fabricated into parts using the Renkforce 1000 printer (Zhang et al. 2020). In addition, solvent debinding, thermal debinding, and sintering were also conducted to densify the printed parts. Representative companies of material extrusion include Stratasys (USA), Markforged (USA), Essentium (USA), Robocasting (USA), and Ultimaker (Netherlands).

Figure 1.1c illustrates the fused deposition modeling process, a representative material extrusion technique. The build material and the support material, in the form of thermoplastic filaments, are heated to the molten state in the nozzles, extruded, and solidified on the build platform. The support structures are removed through mechanical and/or chemical procedures during post-processing.

The PBF technique utilizes a heat source (e.g. electron beam or laser beam) to coalesce metal, polymer, or ceramic powder particles in a powder bed to build 3D objects, and it can theoretically process any powder-based materials on the condition that the corresponding powder particles can be fused or melted through heating. The technique can be categorized into laser powder bed fusion (LPBF) (also widely known as selective laser melting), electron beam melting (EBM), selective laser sintering, multi jet fusion, and high speed sintering processes. LPBF and EBM are mainly employed to print pure metals, alloys, and metal matrix composites (Han et al. 2020a, 2020b), while the selective laser sintering, multi jet fusion, and high speed sintering processes are typically implemented to treat polymers and their composites. Representative commercial companies of PBF include SLM Solutions (Germany), EOS (Germany), Trumpf (Germany), 3D Systems (USA), GE Additive (USA), Renishaw (UK), Bright Laser Technologies (China), and Farsoon Technologies (China).

Figure 1.1d presents a typical PBF process, LPBF, which utilizes a laser beam to selectively melt metal powder particles in the powder bed. The molten metal particles coalesce and solidify to form the printed part. While unmelted powder particles can serve as support, support structures are generally required to be printed to ensure the good printability of overhanging structures of a part.

The DED technique utilizes a laser beam, an electron beam, or an electric arc to melt metal powders or wires upon their deposition along the printing paths (Birmingham et al. 2015; Li et al. 2021). The technique includes processes such as laser-based directed energy deposition (L-DED) (also widely known as laser engineered net shaping and laser metal deposition), laser wire additive manufacturing (LWAM), wire arc additive manufacturing (WAAM), and electron beam freeform fabrication (EBF³, also known as electron beam AM). The L-DED process is commonly employed to print parts using powders, while the other four processes

employ wires for printing. Examples of representative companies for DED include Optomec (USA), Sciaky (USA), DMG Mori (Germany), Trumpf (Germany), BeAM (France), and Bright Laser Technologies (China).

Figure 1.1e illustrates a typical DED process, L-DED, in which metal powder particles are delivered through channels in a nozzle and melted by a laser beam upon deposition onto a freeform substrate. The molten metal particles subsequently solidify to form the printed part.

The binder jetting technique utilizes one or more inkjet printheads to deposit droplets of a liquid polymer binder onto ceramic or metal powder particles in a powder bed and selectively glue them together to build 3D objects (Mostafaei et al. 2017). The droplets can be deposited through a single-pass or multi-pass printing strategy. Post-processing procedures, such as curing, de-powdering, infiltration, and sintering, are often required for green parts printed through this technique. Examples of commercialized companies specializing in binder jetting include Exone (USA), Hewlett-Packard (USA), Desktop Metal (USA), Digital Metal (USA), 3D Systems (USA), Voxeljet (Germany), and Long Yuan (China).

Figure 1.1f demonstrates a metal binder jetting (MBJ) process, in which a layer of metal powder particles is spread by a roller across the build platform, and a liquid binder is then selectively deposited to bond specific regions of the powder layer.

The sheet lamination technique can be employed to fabricate 3D objects by stacking and laminating thin sheets of materials (e.g. paper, metal sheets, ceramic tapes, woven fiber composite sheets, and thermoplastic foils) through different bonding (e.g. adhesive bonding, thermal bonding, and ultrasonic welding) and cutting (e.g. computer numerical control [CNC] milling, laser cutting, and water jet cutting) strategies. According to the ISO/ASTM standard, representative processes of the sheet lamination technique include laminated object manufacturing and ultrasonic AM. Laminated object manufacturing was the first commercialized sheet lamination process and was initially implemented to bond kraft paper. Subsequently, the applicability of this process for bonding plastic/metal tapes and foils has been investigated. Meanwhile, the ultrasonic AM process is commonly utilized for printing parts from metal foils and sheets (Dehoff and Babu 2010). In addition to the two aforementioned processes, a novel sheet lamination process, friction stir AM, is currently in development. In this process, metal plates are utilized as feedstock materials. A stirring pin is inserted into a newly added metal plate at high rotation rates, and the resultant friction between the stirring pin and the plate produces heat that softens and bonds the plate to the previous plate. Representative companies for sheet lamination include Fabrisonic (USA), Evolve Additive (USA), and Impossible Objects (USA).

Figure 1.1g presents a diagram of the sheet lamination process, ultrasonic AM, in which each layer of a metal foil is laid and bonded to the previous layer through ultrasonic welding. This process involves the actuation of a cylindrical sonotrode with an ultrasonic transducer to induce a scrubbing motion of the sonotrode. At the same time, a downward force is applied to the metal foils. The sonotrode rolls along the length of the foils due to the downward force, and ultrasonic vibrations are applied along the width of the foils through the sonotrode. Friction can be produced

between the metal foils through the interaction of the downward force and ultrasonic vibrations. Bonding is achieved through disruption of the oxide layers between the metal foils utilizing friction, thereby promoting nascent metal-to-metal contact. The metal layer is subsequently cut through CNC milling to obtain the desired geometry, and the cycle is repeated until the metal part is completed.

1.3 Metal Powder–Based AM

Powder–based AM is an important subset of the AM family for manufacturing parts using powders as feedstock materials, and it employs the PBF, DED, and binder jetting techniques. In particular, LPBF, EBM, L-DED, and MBJ are commonly adopted powder–based AM processes for printing metal parts. LPBF, EBM, and L-DED share similar features, such as the usage of high-energy heat sources, localized melting, and microstructural evolution upon solidification. Applying metal powder–based AM in producing structurally sound, defect-free, and reliable parts requires an in-depth understanding of existing printing techniques, the physical and chemical processes involved during printing, feedstock materials, process control methods, and underlying mechanisms of common defects and their prevention.

Metal powder–based AM excels in the following aspects: (i) its ability to recycle feedstock materials, (ii) its relatively high manufacturing accuracy as compared to wire- and sheet-printing, and (iii) the capacity of certain powder–based AM processes (MBJ and EBM) to print parts without requiring support structures because of the support provided by the surrounding unfused or partially melted powder particles. Notably, metal powder–based AM plays an indispensable role in various domains, including the aerospace, biomedical, automotive, molding and tooling, energy, jewelry, marine, oil and gas, and repair and remanufacturing industries.

1.4 Post-Processing

It is challenging to employ metal powder–based AM to directly fabricate parts with properties and surface characteristics that satisfy application requirements. Most metal powder–based AM techniques require post-processing treatment to obtain the desired properties in the printed parts (ISO and ASTM International 2015). Post-processing is crucial for addressing the main issues of AM parts, such as high surface roughness, high porosity, dimensional deviations with respect to the models, and substandard mechanical properties for industrial applications.

In certain metal powder–based AM processes (PBF and DED), a metal substrate where parts can be printed onto is often required. Therefore, the post-processing process of wire cutting, typically using electric discharge machining (EDM) which generates a pulse discharge between a tool electrode and a target object (comprising printed parts and the substrate) for cutting, is required to separate the printed parts from the substrate. This process is also commonly employed to assign desired geometries to printed parts for various purposes (e.g. tensile, fatigue, or fracture toughness testing).

Table 1.2 Post-processing for metal powder-based AM.

Categories	Representative techniques
Surface quality improvement	Manual grinding Machining Sandblasting Shot peening Mechanical polishing Chemical polishing Chemical etching Laser shock peening Laser polishing
Residual stress relief and defect reduction	Stress relief annealing Hot isostatic pressing
Aesthetic improvement	Spray painting Electroplating

Table 1.2 exhibits representative post-processing techniques for metal powder-based AM. In accordance with their respective objectives, these techniques can be classified into the categories of surface quality improvement, residual stress relief and defect reduction, and aesthetic improvement.

1.4.1 Surface Quality Improvement

Printed metal components typically undergo post-processing treatment to improve their surface quality (i.e. reduction in surface roughness), which includes manual grinding, machining, sandblasting, shot peening, mechanical and chemical polishing, chemical etching, laser shock peening, and laser polishing.

Manual grinding typically involves abrasive sandpapers with different grit sizes. However, such treatment is only applicable for prototypes or small batches of parts due to its low repeatability and high dependence on the skill of the operator. In addition, any support structures attached to the parts (e.g. overhangs) should first be removed before the grinding process.

Machining utilizes power-driven machines and cutting tools to reduce the surface roughness of printed parts. In particular, CNC is a commonly adopted precision machining process characterized by stable machining quality and high flexibility, machining accuracy, and productivity. Notably, CNC allows for the customization of control programs in each working task to establish control over various tools (e.g. lathes, milling machines, and grinders) in reducing the surface roughness of printed parts.

Sandblasting is the process of removing rust, oxides, and oil contaminants from a surface with high-speed sand (e.g. copper ore sand, emery sand, quartz sand, or iron sand) propelled by compressed air. Sandblasting operations can be categorized

into dry-type sandblasting and liquid blasting processes. The dry-type sandblasting involves pure abrasive propellants capable of removing large amounts of surface material without contamination. In contrast, liquid blasting utilizes a mixture of abrasives and liquid, which removes only small amounts of material but introduces contamination to the parts.

Shot peening is a cold working process that bombards the surface of a material with a stream of small shots (i.e. spherical particles of metal or ceramic) with controlled intensity and coverage. It can increase surface hardness and extend the service life of a part by creating an induced compressive stress layer to enhance its fatigue resistance. Additionally, the surface roughness of printed parts can be reduced and their surface grains can be refined. The shot peening process is commonly performed using air blast systems or centrifugal blast wheels.

Polishing is the process of creating a smooth and specular surface through mechanical or chemical methods. Mechanical polishing methods include magnetically driven abrasive polishing, hydrodynamic cavitation abrasive finishing, and ultrasonic cavitation abrasive finishing.

Magnetically driven abrasive polishing utilizes a slurry comprising magnetic and abrasive materials in a viscous liquid to polish a surface. Hydrodynamic cavitation abrasive finishing is a novel surface modification process employing hydrodynamic cavitation along with abrasives to remove surface irregularities and decrease the surface roughness of a workpiece. In ultrasonic cavitation abrasive finishing, the application of ultrasound and micro-abrasives produces a synergistic effect, in which the former induces the cavitation effect to remove partially melted powder particles on a surface, while the latter serves as bubble nucleation sites to increase the overall cavitation intensity, which further contributes to gradual surface erosion through high-velocity abrasive collisions.

In chemical polishing, a ground sample is immersed in a polishing agent or swabbed with a chemical solution until a clean surface is obtained. Electropolishing is a representative electrochemical polishing process for producing smooth surfaces, and it is accomplished by creating an electrochemical cell in which the printed part is charged anodically. A varying current density is established across the material surface, and it is higher at the peaks and lower at the valleys of the surface topography. The relatively high current density at the protruding points on the surface causes these sites to rapidly dissolve, which levels the surface. However, the effectiveness of electropolishing is limited by the accessibility of counter electrodes in printed parts containing tight spaces and exhibiting complex geometries.

Chemical etching is a post-processing treatment in which chemical reactions occur at the interface between a printed part and a chemical solution, leading to changes in the former's surface roughness. This approach is particularly applicable for treating printed parts with open porous structures.

Laser-based treatment methods utilize laser sources to remove materials and improve the surface accuracy of AM metal parts. Laser-based treatment includes laser shock peening and laser polishing.

In laser shock peening, a pulsating laser beam is directed onto the surface of a metal part, generating shock waves induced by the ablation of a sacrificial layer on the surface. These shock waves travel throughout the surface layer of the part

to cause surface grain refinement and plastic deformation and induce compressive residual stress, which improves the resistance of a material toward fatigue crack initiation and propagation. The underlying mechanism of residual stress generation is similar to that of conventional shot peening, and plastic compression is achieved by the passage of shock waves.

Laser polishing, also known as laser remelting, can enhance the surface accuracy of AM parts while avoiding ablation. In this process, a high-power laser source irradiates the material surface with low-frequency pulses at high scanning speeds to induce local surface melting on the order of nanometers to micrometers. Laser remelting is an eco-friendly process that can improve surface accuracy and reduce surface porosity without incurring any loss of surface materials.

1.4.2 Residual Stress Relief and Defect Reduction

Parts printed by metal powder-based AM processes such as PBF and DED are often subjected to residual stress, which must be relieved through heat treatment before the parts are suitable for industrial usage. The most commonly adopted heat treatment is stress relief annealing, which is a special annealing process that minimizes the residual stress within printed metal parts. This treatment is conducted by heating the parts to a specific temperature below their recrystallization temperature followed by air-cooling. Low-temperature stress relief annealing has a low impact on the microstructure and mechanical properties of a material (Wang et al. 2016), while high-temperature stress relief annealing may refine grains, produce a low dislocation density, and alter the mechanical properties of a material (Xiong et al. 2017). Therefore, low-temperature stress relief annealing is preferable to high-temperature stress relief annealing because it is desirable not to change the microstructure of printed parts during the annealing process.

Hot isostatic pressing (HIP) heat treatment, a thermomechanical treatment process involving the simultaneous implementation of a high temperature (up to 2000 °C) and high isostatic pressure (up to 200 MPa) in a specially constructed vessel with gas as the pressure-transmitting medium, is employed to reduce the porosity of printed parts and improve their densification. Argon gas is the most common pressure-transmitting medium in HIP. Under a high temperature and pressure, the internal pores within a printed part tend to collapse, thereby leading to its densification.

The principal factor distinguishing HIP from other heat treatment techniques is its use of an inert gas as a pressure-transmitting medium to produce uniform microstructural changes on the part surface. The isostatic pressure in HIP arises from the gas atoms colliding with the surface of the part, during which each gas atom is akin to the hammer in a forge. These atomic “hammers” reliably and consistently reach the entire part surface, which corresponds to a uniform pressure.

1.4.3 Aesthetic Improvement

Aesthetics is an indispensable aspect of printed parts. Therefore, improving the aesthetic quality of printed products can further increase their value. Generally, the

“appearance, anti-corrosion, anti-aging, and anti-slip” properties of parts should be considered. Commonly employed methods for achieving aesthetic improvement include spray painting and electroplating.

Spray painting is a painting technique in which paint particles are atomized and sprayed onto a surface. It includes various methods such as air gun spraying, electrostatic spray painting, airless gun spraying, automated linear spraying, and automated flatline spraying. Spray painting is often utilized to improve the appearance of a printed part by applying a smooth and flat coating of the desired color(s) on its surface.

Electroplating is a process that applies a metal coating on a part by external electric fields. In a salt solution containing the metal, the cations of the metal are reduced to atoms through the electrode reaction, and the atoms are subsequently deposited on the surface of the part (that acts as the cathode) to form the coating. Aside from enhancing the appearance of printed parts, the electroplating process can improve their resistance to oxidation, wear, and corrosion, as well as their electrical conductivity. Metals such as chromium, zinc, copper, and nickel are applicable for electroplating.

1.5 Powder Properties and Characterization Methods

Powders form the basis of powder-based AM, and their quality determines the printability and performance of the final parts. While the Technical Committee 119 of ISO has developed and published numerous standards for powder metallurgy since 1967, no standard defined specifically for powder-based AM exists, and thus previously defined metallurgy standards on powder characterization methods are adopted.

Powder sampling must be conducted before any powder characterization can be performed. Sampling methods include scoop sampling, conical pouring and quartering, and chute splitting. In scoop sampling, a scoop of powder is obtained for sampling. Conical pouring and quartering involve pouring the powder onto a flat horizontal surface and dividing the heap into four samples by a cross-shaped cutter. In chute splitting, a chute splitter is employed for sample division. After sampling, a powder can be characterized in terms of its particle morphology, particle size, particle size distribution, density, flowability, chemical composition, and microstructure.

1.5.1 Particle Morphology

The morphology of powder particles can be determined via a standard glossary developed by the British Standards Institute (British Standards 2955 Glossary of Terms Relating to Powders). Particle morphology, which includes shapes and surface features, is dependent on the preparation processes during powder production. The shape of a particle can be described using the following terms: spherical (globular-shaped), acicular (needle-shaped), angular (sharp-edged or roughly polyhedral-shaped), crystalline (a geometric shape freely developed in liquid), dendritic (branched crystalline-shaped), fibrous (regularly or irregularly thread-like),

Table 1.3 Summary of particle size indices and particle shape indices and their descriptions.

Particle size index	Description
Martin's diameter	Length of the line that bisects the area of the particle image (all particles are measured in the same direction).
Feret's diameter	Maximum length of a particle measured in a fixed orientation.
Projected area diameter	Diameter of a circle with the same area as the 2D image of a particle.
Longest diameter	Maximum diameter of a particle.
Perimeter diameter	Diameter of a circle having the same circumference as the perimeter of a particle.
Maximum horizontal intercept	Length of the longest line that can be drawn through a particle in a fixed direction.
Particle shape index	Description
Elongation factor	Aspect ratio that is the ratio of the side lengths of an enveloping rectangle that has the minimum area around the cross-section of a particle.
Bulkiness factor	Ratio of the area of a projected particle to the area of the enveloping rectangle.
Surface factor	Sphericity that is used to compare the surface of a particle and the surface of a sphere of equivalent volume.

lamellar (plate-like), granular (equidimensional but irregularly shaped), irregular (lacking symmetry), or modular (round but irregularly shaped).

Table 1.3 summarizes the particle size indices and particle shape indices that can be used to quantitatively describe the morphology of a particle (Allen 1997). Figure 1.2 presents representative surface features and defects of powder particles, which include “splat caps”, pores, elongated shapes, breakage, agglomeration, irregular shapes, and small satellites (Mostafaei et al. 2021).

The morphology of powder particles can be characterized by optical microscopy and scanning electron microscopy (SEM). Optical microscopy allows for the counting and measurement of particles at maximum magnification values ranging from 500 to 1500, depending on the model of the apparatus used. Meanwhile, a typical SEM is applicable for imaging surface features with a magnification of up to 3×10^6 and at a resolution of tens of nanometers, thereby enabling the evaluation of grain sizes and second phases on unetched surfaces. Furthermore, when equipped with a backscatter electron detector, an SEM device can facilitate the observation of microstructures on unetched surfaces.

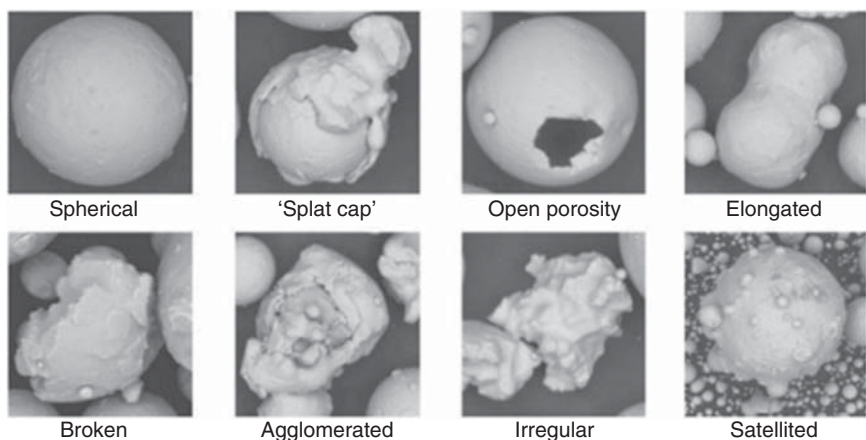


Figure 1.2 Micrographs of powder particles exhibiting various surface features and defects. Source: Mostafaei et al. (2021)/reproduced with permission from Elsevier.

1.5.2 Particle Size Distribution

The particle size distribution of an AM powder is one of its most important characteristics. A volume distribution with respect to particle size can be plotted, as shown in Figure 1.3. The area under the distribution curve to the left of the vertical line $x = D_i$ corresponds to the percentage of the total powder particles that are of sizes smaller than or equal to a specific size gauge D_i . For example, $D_i = 20 \mu\text{m}$ indicates that $i\%$ of all particles are smaller than or equal to $20 \mu\text{m}$. The size gauges D_{10} , D_{50} , and D_{90} are the most commonly used indicators. The span, given by $(D_{90} - D_{10})/D_{50}$, is sometimes selected to represent the width of a Gaussian particle size distribution. Additionally, the mean, median, and mode of a particle size distribution, which

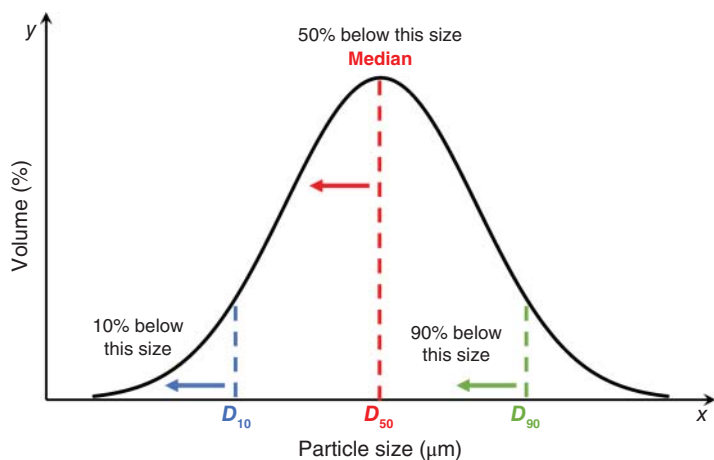


Figure 1.3 Particle size distribution curve showing the size gauges D_{10} , D_{50} , and D_{90} .

correspond to the average particle size, D_{50} , and the peak of the distribution curve, respectively, can be determined.

Particle size distribution is typically measured by the laser diffraction method. This method serves as a convenient and rapid analysis for a broad range of particle sizes. A typical laser diffraction measuring instrument contains a laser source, a particle dispersion module, a particle delivery module, and a detector. When the laser beam is blocked by a particle, part of the light scatters. An angle between the propagation direction of the original and scattered light is formed. A larger particle size results in a smaller angle. Upon being illuminated by parallel laser beams, particles of the same size in a sample deflect light at an identical angle. The scattered light is directed onto a sensor located on its focal plane, forming a series of concentric rings. The intensity of each ring, which corresponds to a specific angle of scattering, is measured to evaluate the volume size distribution of the constituent particles of the sample.

The particle size distribution of a sample can also be quantitatively measured from images captured by optical microscopy or SEM. The images of the constituent particles are usually post-processed before their equivalent diameters are determined, and the entire procedure may be time-consuming. An SEM machine developed by ASPEx Corporation is equipped with an automated feature analysis module, which is capable of quantifying the sizes of thousands of particles within several hours.

Sieve analysis, which involves the separation of particles according to their sizes, is also commonly employed to obtain the particle size distribution of a sample owing to its simplicity and low cost. A typical sieving unit comprises a series of sieves stacked on top of a shaker exhibiting rotary and tapping motions, with each sieve incorporating a phosphor bronze or stainless steel wire mesh cloth woven in a square mesh pattern. The sieves are stacked in the order of decreasing mesh sizes, with the sieve possessing the largest mesh size on top. Standard sieve sizes are specified in ISO standards 565 and 3310/1, ASTM standard E 11, and CIS standard GOST 3584.

1.5.3 Density

The packing density of a powder bed is defined as the ratio of the volume of its constituent powder particles to its total volume. It is a key parameter for assessing the packing efficiency of a powder bed in AM. A powder bed with a large packing density minimizes the porosity of the printed parts, thereby improving their mechanical properties. The packing density of a powder bed is influenced by a variety of factors such as the characteristics of the powder particles (size, size distribution, and shape), bulk properties (e.g. Young's modulus and hardness), and powder spreading parameters (powder layer thickness and spreading velocity). For bimodal powder mixtures containing both small and large particles, the maximum packing density can be achieved with specific ratios of the two types of powder particles, as shown in Figure 1.4.

The apparent density of a powder, with units of g/cm^3 , is defined as the mass per unit volume of its loose powder particles. The Hall funnel method is the most prevalent method for measuring the apparent density of a powder, and the powder is

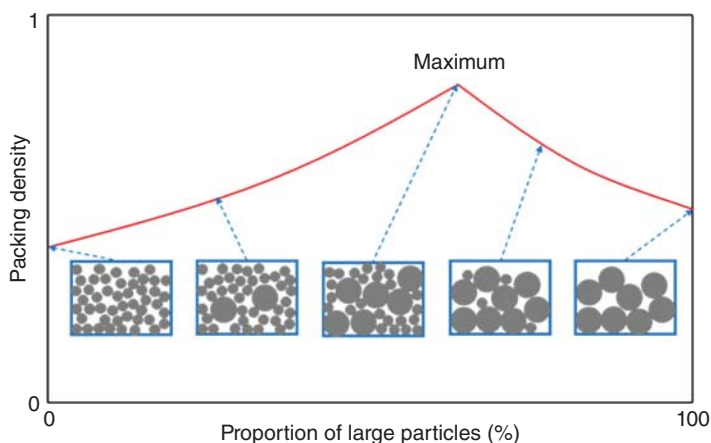


Figure 1.4 Variation of the packing density with the proportion of large powder particles for bimodal powder mixtures. Source: Adapted from German (1992).

poured through a funnel to fill a 25 cm^3 container. The apparent density is obtained by dividing the mass of the contents in the container by its volume. Generally, the apparent density of a powder decreases with its particle size and increases with its particle surface roughness. A powder with a wide size distribution possesses a relatively high apparent density since the space between its coarse powder particles is filled by smaller powder particles.

The tap density of a powder is defined as its density when its container is tapped or vibrated under specified conditions. The tap density (unit: g/cm^3) of a powder is obtained by dividing the mass of the tapped powder in a container by its volume. ISO 3953 established a method for measuring the tap density of a powder, in which a 100 ml (with increments of 0.2 ml) glass graduated cylinder is typically utilized. The tap density of a powder is dependent on the size distribution, shape, and surface roughness of its particles and is always higher than the free-flow apparent density.

The skeletal density, which is often measured through pycnometric methods, is the true density of a powder in its solid state. In pycnometry, the ratio of the mass of a powder to its volume is determined based on the volumetric displacement of a fluid medium. Gas pycnometry, in which helium or nitrogen is employed as the fluid medium, is commonly practiced since the tiny gas atoms can occupy the defects within a solid powder. Meanwhile, liquid pycnometry provides an alternative approach in which highly penetrative liquids (ethanol, oils, butanol, acetone, etc.) are selected as the fluid medium. The number of defective powder particles exhibiting cracks, satellite particles, and pores can be estimated based on the measured skeletal density of a powder.

1.5.4 Flowability

The flowability of a powder is often construed as its ability to flow in a desired manner. In powder-based AM systems, flowability determines the feeding and spreading

behaviors of a powder. It is influenced by the particle size distribution, density, particle morphology, and moisture content of the powder. For example, fine powder particles (smaller than $10\ \mu\text{m}$) typically flow poorly and may even become stuck, while a powder that contains both fine and large particles exhibits good flowability. Due to its relative ease of measurement and correlation to powder flow behaviors, the Hausner ratio of an AM powder, expressed as its tap density divided by its apparent density (Hausner 1967), is commonly used to quantify its flowability. Since both the apparent and tap densities are related to interparticle friction, the Hausner ratio also represents interparticle friction, which directly influences flowability. Generally, a Hausner ratio smaller than 1.25 corresponds to a free-flowing powder.

The flowability of a powder can be assessed based on its flow time, which is defined as the duration for 50 g of the powder to flow through a funnel with a 2.5 mm diameter opening under the influence of gravity (Hall flowmeter). The flow time of a powder is expressed in units of g/s and can be readily compared with those of different powders for a quick assessment of its flowability. Another common flowability parameter is the angle of repose α , which is defined as the angle between a horizontal surface and the slope of a powder heap (Figure 1.5). To measure this parameter, a powder is allowed to fall freely, typically through a fixed funnel, and deposited onto a horizontal surface. Similarly to the Hausner ratio, the angle of repose is related to interparticle friction and cohesion, and a large angle of repose indicates poor powder flowability.

Spherical powder particles usually exhibit better flowability than their irregularly shaped counterparts. A high moisture content can increase powder stickiness and reduce powder flowability. Therefore, it is recommended to dry the powder before printing. Although the flowability of a powder is mostly an intrinsic property, it is also dependent on the interactions between the powder and the environment of AM systems. The interactions between a powder and various AM systems thus contribute to different powder flow behaviors. Therefore, extensive testing with respect to different AM equipment is necessary to evaluate powder flowability.

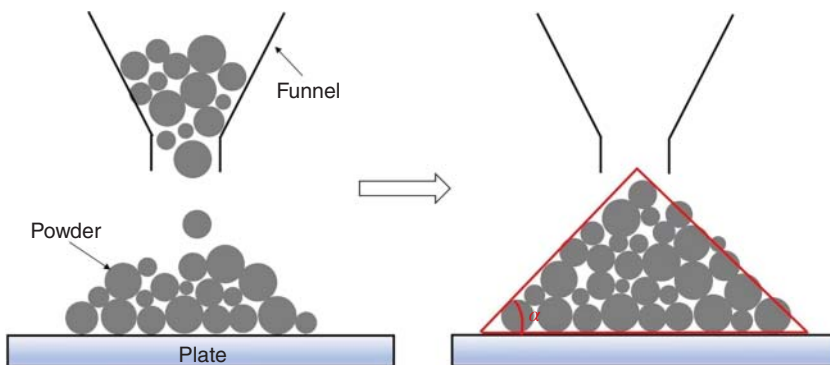


Figure 1.5 Schematic of a fixed funnel method for measuring the angle of repose of a powder.

1.5.5 Chemical Composition

The chemical composition analysis of a powder involves both surface and bulk analyses. Surface analysis methods include energy dispersive spectroscopy (EDS), electron probe microanalysis (EPMA), auger emission spectrometry (AES), X-ray photoelectron spectrometry (XPS), and secondary ion mass spectrometry (SIMS). Meanwhile, bulk analysis methods cover atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectroscopy (ICP-AES), X-ray fluorescence (XRF), infrared (IR) spectroscopy, and inert gas fusion. These two categories of analytical methods are further elaborated in the following subsections.

1.5.5.1 Surface Analysis Methods

When coupled with SEM, EDS can be utilized to identify chemical compositions on the microscale and evaluate the chemical composition on a particle surface. Since a SEM/EDS system requires conductive samples, this method is more suitable for evaluating the particle size and chemical composition of metal powders than polymer powders. Meanwhile, EPMA provides qualitative and quantitative analyses for elements with atomic numbers greater than or equal to 11 (Na) with detection limits of approximately 1 μm . However, the detection sensitivity of EPMA is relatively poor for light elements with atomic numbers ranging from 5 (B) to 10 (Ne).

AES can facilitate the compositional analysis of almost every element (except H and He) on a powder surface with a sensitivity of 0.1–1.0 at.%. Meanwhile, XPS, a surface-sensitive quantitative spectroscopic method based on the photoelectric effect, can be conducted in tandem with ion-etching to identify the elements constituting the surface of a material and their chemical states, as well as the overall electronic structure and density of electronic states within the material. Finally, a variety of information pertaining to the surface, subsurface, or bulk composition of a powder can be acquired through SIMS, with a detection limit in the parts per billion (ppb, in units of ng/ml^3) to parts per million (ppm, in units of $\mu\text{g/ml}$) range for elements.

1.5.5.2 Bulk Analysis Methods

The AAS method is one of the most commonly employed methods for trace element analysis. It is capable of detecting the element content in a powder with a detection limit in the ppb range. This method is established based on the transition of higher orbital electrons of a gaseous atom from the ground state to an excited state upon absorbing radiation of a specific wavelength. Thus, it can qualitatively and quantitatively analyze an element based on its absorption spectra with respect to a ground-state atomic vapor.

ICP-AES can detect over 70 elements (not Ar), with detection limits ranging from the ppm to ppb range, with most samples being aqueous solutions at higher levels of accuracy. This method utilizes plasma as an excitation light source, and multiple elements can be detected simultaneously. In an ICP-AES system, the sample is first atomized and subsequently enters a plasma channel in the form of an aerosol. Finally, the aerosol sample is fully vaporized, ionized, and excited in

a high-temperature inert atmosphere, thereby emitting radiation corresponding to the characteristic spectra of its constituent elements, from which the element content can be determined.

XRF is an efficient and nondestructive method that employs high-energy X-rays or gamma-rays to bombard a sample and induce the emission of secondary X-rays characterized by its constituent elements. These secondary X-rays are captured by a detector installed within an XRF system, which converts such signals into useful information regarding the element content of the sample. This method has a resolution limit of approximately 100 ppm.

IR spectroscopy is usually performed to identify functional groups in organic molecules, and the samples can be in the form of solids, liquids, or thin films. In the sample, molecular vibrations, in the form of stretching and bending of covalent bonds, occur at specific frequency values, which correspond to troughs in the IR spectra. Specific chemical bonds and functional groups in the sample are identified based on these troughs. IR spectroscopy has also been employed to characterize surface oxides on metal specimens (Jasinski and Iob 1988). Oxidation of a powder, particularly metal powder, is detrimental to powder-based AM processes. When a metal powder melts during the printing process, oxide layers form on the powder surfaces due to oxidation and hinder the consolidation of the printed parts, thereby resulting in the so-called “balling effect”. Hardened oxide films also impede proper surface wetting and lead to poor adherence of the printed layers, which may induce porosity in the printed parts. Another type of powder contamination exists in the form of hydroxide films, which typically form on powder surfaces due to their ability to absorb moisture under high humidity. In contrast to solidified oxide layers that are often hard and brittle, hydroxide films are generally highly viscous. Therefore, the hydroxide films increase the tendency of particles to agglomerate and inhibit particle flow within the powder bed. Finally, irradiation of water layers adsorbed onto powder surfaces facilitates the dissociation of hydrogen atoms from the water molecules, and entrapped gas pores are formed upon the solidification of the melt pool, causing melt pool sputtering.

Inert gas fusion is a quantitative method for measuring the contents of H, N, and O elements in metal samples (Holt and Goodspeed 1963). Samples are first weighed and placed in a graphite crucible, in which they are heated to a molten state. Meanwhile, H_2 , N_2 , and O_2 molecules released from the samples are separated to evaluate the weight percentage of each element.

1.5.6 Microstructure

X-ray diffraction (XRD) is an X-ray spectrographic method primarily for identifying crystal structures and properties, including the number of phases in a metal powder sample, with a sensitivity of 3–5 vol.% for each phase component. During XRD analysis, a sample is bombarded with X-rays at different incident angles θ , and the intensity of the diffracted X-rays is measured. Constructive interference of the diffracted X-rays results in the formation of distinguishable intensity peaks. The condition for constructive interference to occur is described by Bragg’s law, $n\lambda = 2d\sin\theta$,

where n is the diffraction order (an integer), λ is the wavelength of the incident radiation, and d is the spacing between successive crystal planes (Skoog et al. 2006). By incorporating the knowledge of reflection angles for specific phases and indexing the positions of the peaks, the crystal structure of a sample can be determined.

Focused ion beam (FIB) microscopy is a technique for imaging and milling material surfaces, in which a beam of cations is utilized to form a raster image of a surface or to remove layers from it. Typically, a dual FIB/SEM approach is adopted for powder characterization, in which the FIB setup is mainly employed for milling purposes. Such an approach can also be undertaken to directly visualize the internal grain structure and porosity of powder particles.

Transmission electron microscopy (TEM) is a highly effective analytical tool for imaging a phase in powder form to obtain specific information (size and shape of the phase particles, crystallographic orientation, etc.). In TEM analysis, the specimens must be processed to reach a size of less than 100 nm to be electron transparent. Various specimen preparation methods are available, which include bulk preparation by thinning and dimpling and final polishing by an ion polisher or via electropolishing. A more advanced method for preparing TEM samples is to conduct FIB microscopy in conjunction with SEM to retrieve a sample from a bulk specimen, which is subsequently attached to a copper or molybdenum grid that can be inserted into the TEM facility. The obtained TEM diffraction patterns can be used to determine whether a material is a single crystal (sharp diffraction patterns), polycrystalline (diffraction rings), or amorphous (hazy rings).

Electron backscatter diffraction (EBSD) is a scanning electron microscope-based microstructural-crystallographic characterization method commonly employed when studying crystalline or polycrystalline materials. This method can provide details on the structure, crystal orientation, phase, and strain in powder materials. During an EBSD measurement, a flat and polished crystalline specimen is placed at a largely tilted angle (about 70° relative to the normal incidence of the electron beam) in an SEM chamber. A camera, equipped with a phosphor screen and integrated with a digital frame grabber, is inserted into the chamber and approaches the surface of the inclined specimen. The sample is then bombarded by electrons, which may backscatter and exit at various Bragg's angles, thereby undergoing diffraction and forming Kikuchi bands corresponding to different diffracting crystal planes of the lattice. As a result, the microstructural maps of the sample, which spatially describe its crystal orientation, can be obtained and utilized to examine the micro-texture of the sample. Such maps provide abundant information about a sample, such as its grain orientation, grain boundary, and grain size distribution. Additionally, various statistical tools can also be used to evaluate the average misorientation, grain size, and crystallographic texture of the sample.

Thermal analysis methods are mainly employed for tracking changes in the chemical properties of a sample over a range of temperatures, and they include thermogravimetric analysis (TGA), differential thermal analysis (DTA), and differential scanning calorimetry (DSC). These methods also reveal information regarding the exothermic and endothermic events that occur within the sample. In TGA, the mass of a sample is recorded as a function of temperature, which provides information

on its content according to the loss of volatile elements and the potential formation of oxides. In addition, TGA allows for *ex situ* analysis of the response of a powder subjected to increasing temperatures during PBF processes. Meanwhile, DTA is a qualitative method in which a sample and an inert reference material are simultaneously heated, and the temperature difference between them is recorded as a function of temperature or time, which can be used to identify potential phase transitions. Generally, DTA analysis is also complemented by TGA and DSC. Finally, DSC is a quantitative method that records the difference in heat capacity between the sample and a reference material as a function of temperature.

1.6 Challenges and Future Trends of Metal Powder-Based AM

Present challenges and future trends of metal powder-based AM are centered on developing printing materials and processes, *in situ* monitoring, numerical simulations, and standardization.

The main challenges surrounding the development of printing materials are present in the following aspects: (i) tuning the powder composition to achieve the desired properties of the final parts (e.g. multifunctional, strong, ductile, and lightweight); (ii) controlling the stresses and distortion within the printed parts; (iii) achieving a comprehensive understanding of metallurgical principles; (iv) tuning microstructures and properties in different regions of a printed part by manipulating process parameters and ensuring reproducibility; (v) reducing anisotropy in the mechanical properties of the printed parts; (vi) preventing the formation of metallurgical defects; and (vii) establishing a database of printable materials. In addition, the lack of specialized metal powder preparation processes hinders the standardization of AM powder properties (see Chapter 2 for further details).

Large-scale manufacturing, hybrid manufacturing, and multiple-energy-source-aided manufacturing are projected to be popular future research trends concerning the development of printing processes. For example, large-scale PBF manufacturing utilizes multiple laser sources and optical systems to fabricate parts extensively. Hybrid manufacturing refers to the integration of a powder-based AM technique (PBF or DED) with a subtractive manufacturing system (e.g. milling or grinding), offering a significant improvement of the printed parts in terms of their dimensional accuracy and surface quality. Multiple-energy-source-aided manufacturing incorporates external energy fields (e.g. electromagnetic fields, ultrasonic fields, and electric fields) into a powder-based AM system. Such energy fields induce strong vibrations within the melt pools during the printing process, which can effectively refine the microstructures of the printed parts and reduce metallurgical defects within them.

The challenges of quality control during printing processes primarily lie in the areas of *in situ* monitoring, process sensing, and adaptive control, which are critical in regulating such processes to achieve high productivity while avoiding common defects in the printed parts. For example, a key aspect of process control is the availability of well-tested real-time models that serve as media for relating the process

variables with the desired properties. Notably, adequately standardized phenomenological modeling can reveal the most important factors that affect the quality of metal parts, such as temperature and velocity fields, cooling rates, and solidification parameters. Therefore, it is a powerful tool for assessing the effects of process variables on part quality prior to production. Furthermore, the development and testing of phenomenological models provide a solid foundation for the eventual construction of digital twins of physical objects in metal powder-based AM. With the incorporation of genetic algorithms and other global search algorithms, the utility of such digital twins can be greatly expanded to tailor part attributes, optimize production variables, reduce defects, and improve part quality. However, refining such virtual representations requires considerable time, effort, and resources.

Contemporary numerical simulations of AM are primarily conducted to provide insights on powder-spreading behaviors on the powder bed and heat transfer phenomena, residual stress development, distortion, microstructure evolution, and porosity formation in AM parts. However, there appears to be a lack of agreement regarding the characteristics of an acceptable model since the efficacy of each model is assessed according to its computational cost and/or the accuracy of its corresponding results. Such criteria are difficult to implement due to the different resources available in each research project and the variations between model outputs.

AM modeling research is directed at understanding the underlying mechanisms governing different phenomena, developing a computational model for describing specific processes, and establishing a process–structure–property relationship. One should note that adopting a feedback-based approach is necessary, in which earlier simulation results are utilized in subsequent simulations until a model has successfully satisfied specific requirements (low distortion, desired microstructure, high cycle fatigue, etc.).

Material–structure–performance integrated AM could be explored to achieve high-performance and multifunctional AM parts (Gu et al. 2021). Such technology relies on developing more digitized materials and structures, which could be accomplished with the Materials Genome Initiative, standardization of formats, and a systematic printability database. High mechanical performance and multifunctionality can be simultaneously achieved for an AM metal part through the innovative design of materials and structures.

The standardization of metal powder-based AM is impeded by critical challenges spanning many aspects, which include cost, design, software, materials, traceability, machine constraints, printing process monitoring, mechanical properties, repeatability, scalability, validation, standards, quality, inspection, post-processing, and tolerances. A primary challenge is the unsatisfactory development of qualification and certification process for various AM applications because of high costs, long lead times, and inadequate standards, rules, and regulations. Other challenges arise due to the lack of *in situ* measurements for real-time closed-loop process control systems, insufficient data, and poor process reliability and repeatability due to limited research on heat source–powder interactions, heat transfer, vaporization, defect formation, quantitative metallography, etc. Moreover, the large-scale production of AM parts using commercially available AM equipment is highly difficult.

While the market expansion of AM technologies requires increased standardization and improved quality control of AM products, a more comprehensive understanding of the printing processes and practical innovations must first be achieved.

Despite being a revolutionary method for facilitating customized part fabrication and niche applications, metal powder-based AM requires further research and development to achieve the mass production of parts at a reduced cost.

1.7 Summary

This chapter briefly discusses the development of AM technology, popular metal powder-based AM techniques, post-processing methods, representative metal powder characteristics and their characterization methods, and challenges and future trends of metal powder-based AM.

AM technology is classified into seven broad categories, i.e. vat photopolymerization, material jetting, material extrusion, PBF, DED, binder jetting, and sheet lamination techniques. Among them, PBF, DED, and binder jetting are the predominant powder-based AM techniques. In particular, LPBF, EBM, L-DED, and MBJ are the most commonly adopted powder-based AM processes for printing metal parts.

Most metal powder-based AM products require post-processing to obtain the desired properties. Surface quality improvement methods include manual grinding, machining, sandblasting, shot peening, mechanical and chemical polishing, chemical etching, laser shock peening, and laser polishing. In addition, heat treatment methods, such as stress relief annealing and HIP, can be employed to minimize residual stress within the printed parts and reduce their porosity. Finally, aesthetic improvement approaches include spray painting and electroplating.

Powders are the principal component of powder-based AM, and they are characterized in terms of their morphology, size, size distribution, density, flowability, chemical composition, and microstructure. The quality of a powder is determined by these characteristics, which determine the printability and performance of the final parts.

Present challenges and future trends of metal powder-based AM are proposed in terms of developing printing materials and processes, *in situ* monitoring, numerical simulations, and standardization. Furthermore, as a revolutionary method for facilitating customized part fabrication and certain niche applications, metal powder-based AM technologies require further development to mass-produce parts at a reduced cost.

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2

Metal Powder Preparation Processes

The geometrical, physical, and chemical characteristics of a metal powder play vital roles in its printability and the quality of additively manufactured products. For example, the shape, size, and size distribution of powder particles influence their flowability and packing density during the powder spreading process. In addition, the laser absorptivity and thermal conductivity of powder particles affect their melting and solidification process during printing. Other important factors include the powder surface roughness, oxidation, impurities, and moisture. All these factors heavily depend on how the metal powder is prepared.

As illustrated in Figure 2.1, commercial metal powders are mainly prepared through atomization, mechanical mixing, reduction process, and powder modification. Some metal powders can be produced via multiple processes. A preparation method is commonly chosen by considering its cost and the physical and chemical properties of the materials involved.

Figure 2.2 shows the morphology of Ti–6Al–4V powder particles prepared through the different processes (Sun et al. 2016, 2017a; Dawes et al. 2015). Some of these processes produce powder particles with spherical or near-spherical shapes. In contrast, others produce irregularly shaped powder particles that require further processing to improve their degree of sphericity, such as plasma spheroidization (see Section 2.4.1 for further details). This chapter focuses on the fundamentals and characteristics of the preparation processes of metal powders for additive manufacturing (AM) purposes. Furthermore, it provides a comprehensive understanding of the relationships between the preparation processes and the powder properties.

2.1 Atomization

Atomization is the most widely adopted process for the mass production of pre-alloyed powders for AM. It typically includes gas atomization, water atomization, plasma atomization, and the plasma rotating electrode process. The fundamental principle of atomization is the utilization of a high-pressure gas jet or water stream, or rotating forces to disperse a stream of molten metal into droplets, which solidify to form spherical powder particles. Overall, this process involves melting, atomization, and solidification.

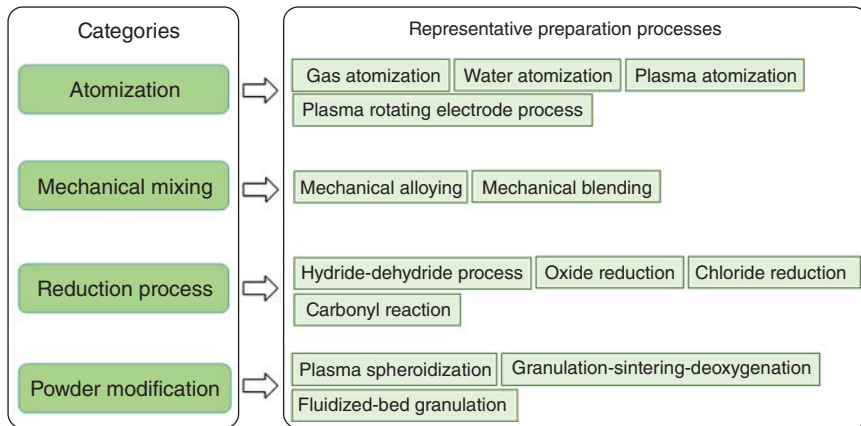


Figure 2.1 Overview of the preparation processes for metal powders.

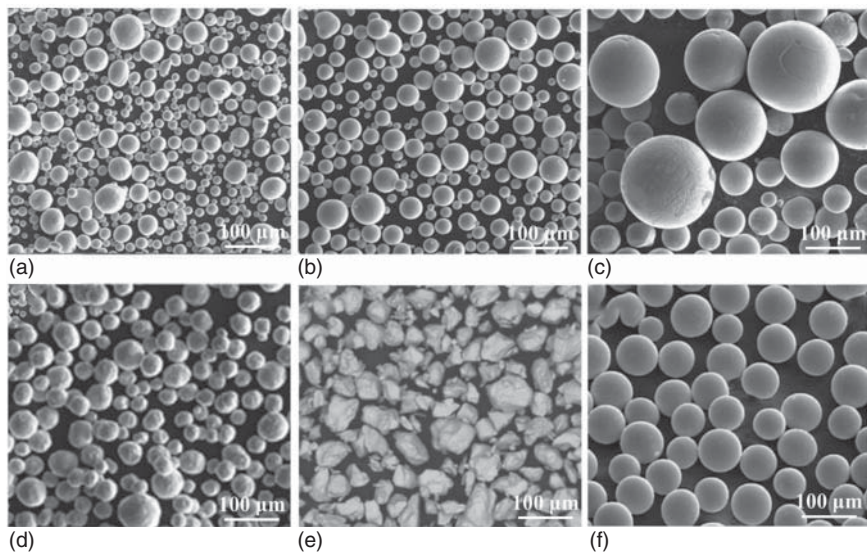


Figure 2.2 SEM images showing the morphology of Ti-6Al-4V powder particles produced through different processes. (a–c) Gas atomization, plasma atomization, and the plasma rotating electrode process, respectively. Source: Sun et al. (2017a)/reproduced with permission from Springer Nature. (d) Oxide reduction. Source: Sun et al. (2016)/reproduced with permission from Elsevier. (e) Hydride–dehydride process. Source: Dawes et al. (2015)/reproduced with permission from Johnson Matthey Plc. (f) Plasma spheroidization. Source: Sun et al. (2017a)/reproduced with permission from Springer Nature.

2.1.1 Gas Atomization

Gas atomization is the most extensively applied process for the production of fine metal powders for AM, e.g. ferrous alloys, titanium alloys, nickel alloys, aluminum alloys, copper alloys, cobalt alloys, magnesium alloys, tin alloys, titanium–aluminum alloys, high-entropy alloys (HEAs), metallic glasses, and

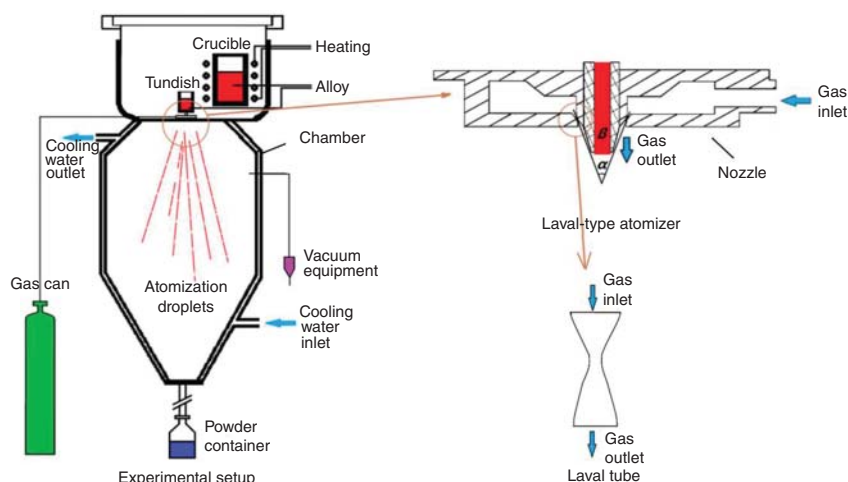


Figure 2.3 Schematic diagram of gas atomization. The parameter α is the angle of the nozzle airflow, and β is the cone angle of the metal tube. Source: Reproduced from Zheng et al. (2018)/with permission from Taylor & Francis.

pure metals. The underlying mechanism involves converting part of the kinetic energy of a high-velocity gas jet ejected through a nozzle to the surface energy of metal droplets disintegrated from molten metal streams. The metal droplets then spheroidize and solidify to form powder particles.

A schematic of the experimental setup for gas atomization is illustrated in Figure 2.3 (Zheng et al. 2018). A typical equipment setup for gas atomization consists of a gas supply system, a melting system, a nozzle, an atomization chamber, a powder collection container, and a gas extraction system (Ünal 2006). First, alloy or pure metal ingots are melted in a crucible, and the molten material is transferred to a tundish from which it is dispensed as a molten stream. Subsequently, the stream is disintegrated into metal droplets by a high-velocity gas using an atomizer. At this stage, the impact between the gas and the stream creates a shockwave that breaks down the molten stream into metal droplets. Finally, the metal droplets solidify to form powder particles when they fly onto the chamber wall. During this process, the chamber is filled with inert gas (e.g. argon) to avoid oxidation of the metal droplets. Meanwhile, cooling water is supplied through the chamber walls to maintain the temperature of the chamber. As a result, gas atomization produces high-purity powders with a high degree of sphericity and low oxygen content.

The complicated breakup process of the metal droplets exerts a significant influence on the shape and size of the solidified powder particles. A work by Wei et al. (2017) presented the breakup process of TA15 titanium alloy droplets during electrode-induction-melting gas atomization. The TA15 droplets first formed oval molten pieces due to the complex mechanical effect of the high-velocity gas. Then, thin molten flakes were decomposed into anomalous molten bands due to the surface tension of the liquid. After further liquid contraction, regular molten sticks were produced. Finally, most regular molten sticks were decomposed into

fine spherical powder particles according to the “normal necking down mode”. Besides, a few molten sticks were transformed into coarse particles according to the “interfere breakup mode”, and a few molten sticks became fine irregular particles according to the “impact breakup mode”. The number of broken metal droplets depends on a dimensionless parameter H (also known as the aerodynamic Weber number), which can be described by

$$H = \frac{\rho_g \mu^2 b}{\sigma_0}, \quad (2.1)$$

where ρ_g is the gas density (kg/m^3), μ is the relative velocity between the gas and the liquid (m/s), b is the characteristic length (m) (typically the droplet diameter), and σ_0 is the surface tension of the liquid (N/m). Therefore, the fracture degree of the liquid flow is greatly dependent on μ and σ_0 .

Provided that the heat transfer between a spherical liquid droplet and the gas medium in the gas atomization process is subjected to Newton’s law of cooling, Yan et al. (2011) showed that the cooling rate of a spherical droplet can be calculated by

$$\frac{dT}{dt} = \frac{6h(T_1 - T_c)}{D\rho_l C}, \quad (2.2)$$

where T is the temperature (K), t is time (s), h is the coefficient of heat transfer, T_1 is the initial temperature of the liquid droplet (K), T_c is the temperature of the cooling medium (K), D is the powder particle size (μm), ρ_l is the density of the liquid (kg/m^3), and C is the specific heat of the liquid (J/kg/K). For a specific material, the size of the powder particle obtained is inversely proportional to the cooling rate. Thus, the particle size distribution of a powder can be tailored through the change in the cooling rate by controlling the atomization process parameters.

The atomization process parameters (such as type of gas, gas pressure, gas flow rate, and gas-to-metal ratio) should be optimized to obtain a metal powder with a high degree of sphericity, a homogeneous distribution of elements, and specific particle sizes as shown in Table 2.1. The gas flow rate generally depends on the gas pressure, temperature, and nozzle cross-sectional area. The gas pressure and mass flow rate are determined by the gas delivery system and hardware. For a particular gas nozzle design, the average particle size of a powder is regulated by the gas pressure and the melt flow rate through the nozzle diameter and suction pressure. A decrease in the melt flow rate may speed up the production of fine powder particles.

Gas atomization has been utilized to produce powders of multi-component alloys, e.g. HEAs and metallic glasses. Figure 2.4a presents an inverse pole map of gas-atomized CoCrFeMnNi HEA powder particles with a mean grain size of $3.6 \mu\text{m}$ based on electron backscatter diffraction (EBSD) analysis (Wang et al. 2019). Dendrite structures rich in Fe, Cr, and Co were observed by energy dispersive spectroscopy (EDS) mapping (Figure 2.4b).

The powder particle size affects the phase and morphology of HEA powders significantly. It was found that gas-atomized $\text{Al}_{0.6}\text{CoCrFeNi}$ powder particles with a minimum size of over $75 \mu\text{m}$ possessed duplex structures consisting of face-centered cubic (FCC) and body-centered cubic (BCC) phases. In contrast, smaller powder particles only formed the BCC phase (Zhou et al. 2018a). The rapid cooling in the case

Table 2.1 Summary of processing parameters for gas atomization.

Powder	Parameters				Average particle size (μm)
	Gas pressure (MPa)	Gas flow rate	Gas-to-metal ratio	Gas type	
Sn alloy ^{a)}	0.2–1.0	27–97 m ³ /h	0.14–0.56	Nitrogen	—
Al alloy ^{b)}	1.4	1.4 Nm ³ /min	—	Nitrogen	—
316L ^{c)}	2.76–6.89	2.75–13.1 kg/min	0.36–1.67	Nitrogen	32.5–34.8
Fe–Ni ^{d)}	2	1.4 Nm ³ /min	—	Nitrogen	48
Al–Si ^{e)}	0.2–0.45	28.62 g/s	0.54–0.74	Nitrogen	60–96
Al–Si10–Mg ^{f)}	2–4	10–54 kg/min	5.32–23.97	Nitrogen	25.67–31.75
Al–Mn ^{g)}	0.4–1.4	—	—	Argon	44–59
TA15 ^{h)}	2–8	—	—	Argon	45
AlCoCrFeNi ⁱ⁾	2.2	—	—	Nitrogen	27
((Fe _{0.6} Co _{0.4}) _{0.75} B _{0.2} Si _{0.05}) ₉₆ Nb ₄ ^{j)}	1.6	513–780 kg/h	1.6–9.6	Argon	35
Mg ₆₃ Zn ₃₂ Ca ₅ ^{k)}	0.4	—	—	—	—

- a) (Lagutkin et al. 2004);
b) (Hong et al. 1999);
c) (Anderson and Terpstra 2002);
d) (Feng and Qiu 2012);
e) (Goudar et al. 2017);
f) (Gao et al. 2019);
g) (Allimant et al. 2009);
h) (Wei et al. 2017);
i) (Yang et al. 2017);
j) (Ciftci et al. 2018);
k) (Zhao et al. 2014).

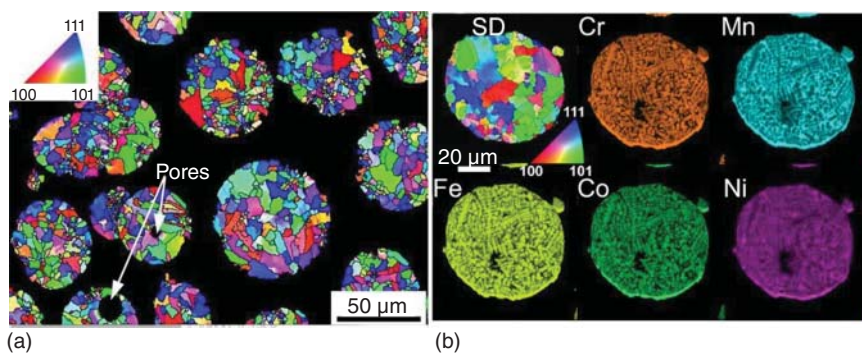


Figure 2.4 EBSD and EDS analysis of CoCrFeMnNi HEA powder particles. (a) The polycrystalline structures of the particles and (b) the corresponding elemental distribution of a particle. Source: Wang et al. (2019)/reproduced with permission from Elsevier, CC BY-NC-ND 4.0.

Table 2.2 Characteristics of Fe–Si–B metallic glass alloy powders produced via gas atomization.

Powder	Particle size (μm)			Apparent density (%)	Tap density (%)	True density (g/cm^3)	Phase
	D10	D50	D90				
$\text{Fe}_{80}\text{Si}_{12}\text{B}_8$	4.1	17.5	75.5	38.9	64.5	7.26	$\alpha\text{Fe}(\text{Si}) + \text{Fe}_2\text{B}$
$\text{Fe}_{75}\text{Si}_{15}\text{B}_{10}$	4.2	17.2	70.9	40.4	69.7	7.04	$\alpha\text{Fe}(\text{Si}) + \text{Fe}_2\text{B} + \text{Fe}_3\text{Si}$
$\text{Fe}_{70}\text{Si}_{18}\text{B}_{12}$	4.1	14.0	48.2	37.1	64.3	6.84	$\alpha\text{Fe}(\text{Si}) + \text{Fe}_3\text{Si}$
$\text{Fe}_{60}\text{Si}_{24}\text{B}_{16}$	3.7	12.8	44.6	38.4	63.9	6.63	$\text{Fe}_{4.9}\text{Si}_2\text{B}$
$\text{Fe}_{50}\text{Si}_{30}\text{B}_{20}$	2.6	10.1	40.2	37.1	64.6	6.33	$\text{FeSi} + \text{FeB}$

Source: Adapted from Alvarez et al. (2018).

of smaller powder particles suppressed the eutectic solidification and improved the solubility of Al in CoCrFeNi to generate the BCC structure. Additionally, a reduction in particle size enhances the powder's surface quality. For example, CoCrFeNiMn powder particles with a maximum size below $53\mu\text{m}$ were observed to possess a higher degree of sphericity and a smoother surface than those with a minimum size exceeding $100\mu\text{m}$ (Park et al. 2018).

The constituent elements and their ratios in an alloy significantly influence the phase composition of HEA powders prepared by gas atomization. For alloys in the AlCoCrFeNi category, an increase in the Al content tends to result in a BCC-dominant structure. The introduction of Si into AlCoCrFeNiCu could accelerate the structural transition from the FCC phase to the BCC phase during gas atomization (Yang et al. 2017). Alloys belonging to the CoCrFeNi category exhibit FCC structures even with the addition of Mn, Mo, and C elements. A high cooling rate (10^4 – 10^5 K/s) is favorable for preventing compositional segregation and restricting the atomic ordering required to generate intermetallic compounds. As a result, gas-atomized HEA powders generally exhibit uniform element distributions and simple microstructures. However, it is difficult to prepare refractory HEA powders using gas atomization because of their extremely high melting temperatures. Spherical refractory HEA powder particles can be prepared through the plasma rotating electrode process as well as milling and thermal plasma spheroidization (for details on the process, refer to Sections 2.1.4 and 2.4.1).

Table 2.2 summarizes the characteristics of $\text{Fe}_x(\text{Si}_{15}\text{B}_{10})_{1-x}$ metallic glass powders prepared by gas atomization (Alvarez et al. 2018). The low apparent density indicated high interparticle friction because of the fine powder particle size. On the contrary, the high tap density showed an efficient vibration packing of the powder particles. The dominant phase in the $\text{Fe}_{80}\text{Si}_{12}\text{B}_8$ alloy was $\alpha\text{-Fe}(\text{Si})$, in which Fe_2B was a minor constituent. A decrease in the Fe content ($\text{Fe}_{75}\text{Si}_{15}\text{B}_{10}$ and $\text{Fe}_{70}\text{Si}_{18}\text{B}_{12}$) resulted in ordered Fe_3Si compounds.

Various gas atomization techniques have been developed by modifying the gas atomizers, such as vacuum-induction-melting, free-fall, close-coupled, electrode-induction-melting, and plasma-melting-induction-guiding gas atomization (Sun

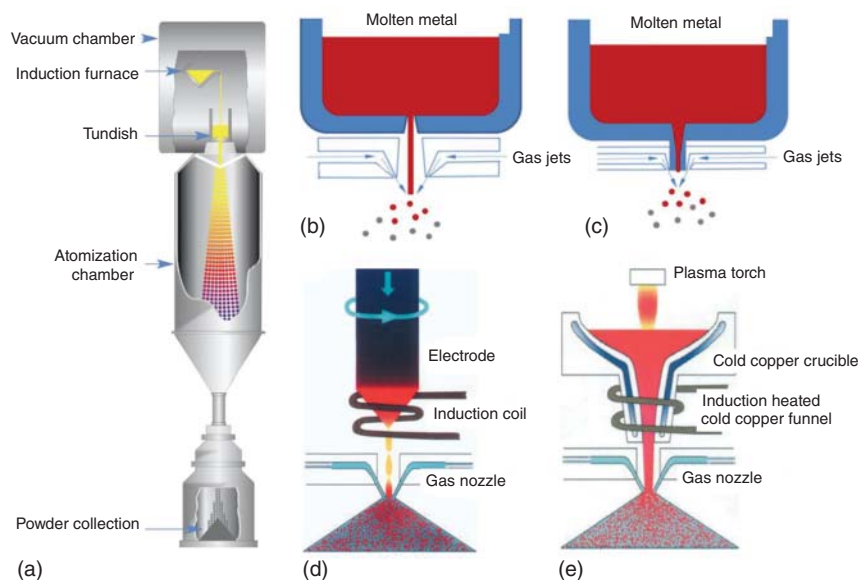


Figure 2.5 Schematic illustrations of different gas atomization techniques. (a) Vacuum-induction-melting. Source: Adapted from Gerling et al. (2004). (b, c) Free-fall and close-coupled processes, respectively. Source: Reproduced from Sun et al. (2017a)/with permission from Springer Nature. (d, e) Electrode-induction-melting and plasma-melting-induction-guiding, respectively. Source: Reproduced from Gerling et al. (2004)/with permission from John Wiley & sons.

et al. 2017a; Gerling et al. 2004). Vacuum-induction-melting gas atomization combined with inert gas atomization is the universal process for preparing nonreactive metal powders with low oxygen content. In this process, a vacuum-induction-melting unit is integrated with an inert gas atomization unit (Figure 2.5a). The feedstock materials are melted through electromagnetic induction, in which electricity is applied to the crucible in a vacuum or an inert gas atmosphere. The molten metal is poured into a tundish when the required melt uniformity and chemical composition have been obtained. Afterward, a fine metal stream is channeled from the tundish orifice to the atomization nozzle, where it is subsequently subjected to a high-pressure gas jet and atomized.

In free-fall gas atomization, a stream of molten metal falls freely under the influence of gravity from the crucible, and it interacts with a gas field generated by the impact of gas jets (Figure 2.5b). At the point of impact, the molten stream breaks into metal droplets that solidify to produce spherical powder particles of various sizes.

Close-coupled gas atomization has been developed to produce metal powders with refined microstructures, extended solid solubility, and amorphous phases. The gas flow in the close-coupled atomizer immediately impacts the exiting molten metal stream (Figure 2.5c). The distance between the gas exit and the melt stream within the close-coupled atomizer is smaller than that in the free-fall atomizer. Therefore, the maximum kinetic energy of the gas can be transferred to a smaller volume of the metal stream. In addition, the close spatial coupling between the gas and the

melt flow can facilitate the rapid cooling of the melt stream at the tip of the atomizer nozzle. Controlling the interactions between the gas and the melt stream using the free-fall design is more convenient than doing so through the close-coupled design. However, it is difficult to control the powder particle size distribution in the free-fall design, which leads to low process efficiency.

The contamination of the produced powders by ceramic particles from the lining of the tundish or furnace poses a critical disadvantage in the abovementioned processes. Therefore, electrode-induction-melting and plasma-melting-induction-guiding gas atomization methods have been developed to prepare high-purity reactive metal powders. The distinction between the two processes lies in the heat source used for melting the feedstock materials. In electrode-induction-melting gas atomization, inductive coils are utilized to melt a pre-alloyed rod electrode that comprises the feedstock metal material. The front-end section of the electrode is melted, and the molten metal is delivered to the gas nozzle for atomization (Figure 2.5d).

Plasma-melting-induction-guiding gas atomization uses a plasma gun to melt metals. The feedstock material is melted in a water-cooled crucible by plasma heat sources (Figure 2.5e). The bottom of the crucible contains a system that directs the molten metal to the gas nozzle while providing additional heating. Therefore, a well-defined melt stream is achieved through this technique.

Figure 2.6 exhibits the morphology of different metal powders prepared by the various gas atomization processes (Singh et al. 2001; Ouyang et al. 2007; Löber et al. 2014; Zhang et al. 2009). Notably, the powders produced by the close-coupled, electrode-induction-melting, and plasma-melting-induction-guiding processes possess a higher degree of sphericity than the powders produced by free-fall gas atomization. However, satellite particles are attached to the surfaces of larger droplets produced by these processes, which reduces powder flowability. The presence of satellite particles can be attributed to the inevitable merging of fine powder with coarser powder. As a result, fine powder particles solidify more rapidly than their coarser counterparts during the atomization processes, and they undergo greater acceleration in the high-velocity gas flow, consequently impacting or welding themselves onto larger molten droplets.

Generally, during gas atomization, the powders produced from alloys with a low density (e.g. aluminum alloys) may have a higher amount of satellite particles than alloys with a high density (e.g. steels). When the droplets of low-density alloys are ejected from the nozzle, their travel trajectories may be more random due to larger acceleration driven by the high-velocity gas flow, which creates a higher chance for finer powder particles to attach onto larger ones to become satellite particles.

Inert gases with higher thermal conductivity (e.g. helium) may be beneficial in facilitating the solidification of fine particles before they impact larger particles to form satellite particles. Nevertheless, argon gas is used instead of helium gas due to the practical cost consideration. Another potential approach for minimizing the formation of satellite particles is to eject the molten metal droplets from the nozzle at supersonic speeds to expedite solidification.

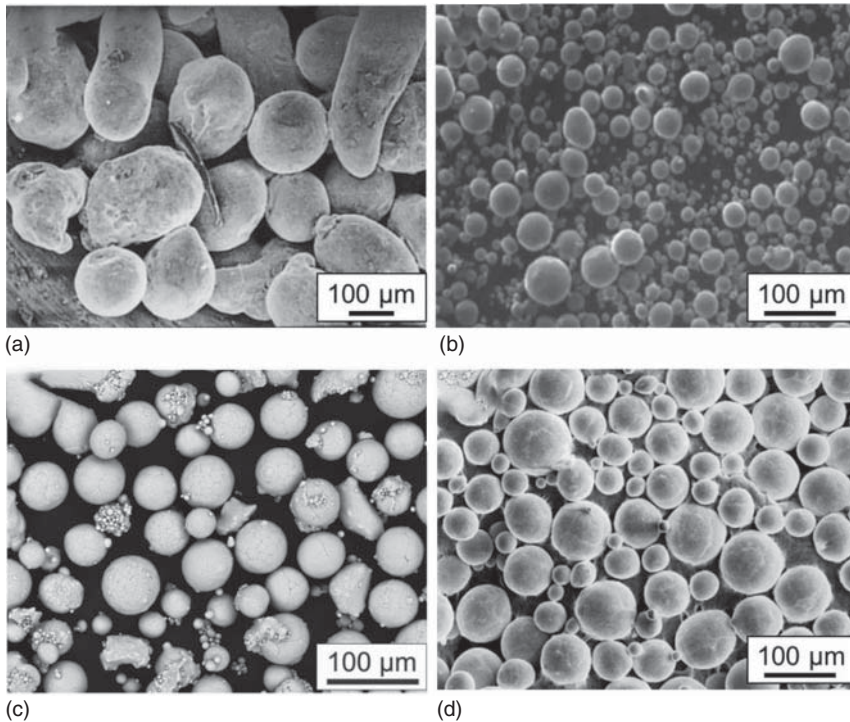


Figure 2.6 Powder morphology produced by different gas atomization processes. (a) Free-fall gas atomization of aluminum powder. Source: Singh et al. (2001)/reproduced with permission from Taylor & Francis. (b) Close-coupled gas atomization of copper powder. Source: Ouyang et al. (2007)/reproduced with permission from Elsevier. (c) Electrode-induction-melting gas atomization of TiAl powder. Source: Löber et al. (2014)/reproduced with permission from Elsevier. (d) Plasma-melting-induction-guiding gas atomization of TiAl powder. Source: Zhang et al. (2009)/reproduced with permission from Elsevier.

2.1.2 Water Atomization

Water atomization is usually cheaper than other atomization methods due to the lower cost of the atomization medium (water), the lower energy used for pressurization compared to gases, and the ability to achieve very high productivity. Water atomization mainly produces ferrous metal powders, such as stainless steels, tool steels, and soft magnetic powders. However, it is also sometimes used to produce nonferrous metal powders, such as copper, nickel, and their alloys, as well as precious metals.

Low powder purity and irregular powder particle shapes are the main limitations of water atomization, particularly for water-reactive metals (e.g. aluminum and magnesium alloys), pure metals, and oxidation-sensitive metals. Nevertheless, at a high cooling rate, the surface oxides of water-atomized powder could be reduced to an average thickness comparable to that of gas-atomized powder (Neikov et al. 2004). In addition, water atomization is generally not used for pure metals and alloys with

a melting point below 500 °C, as the ultrarapid solidification process does not provide enough time for the metal droplets to become spherical after they are ejected from the nozzle (Eisen et al. 1998). Consequently, these metal particles have highly irregular shapes, which are undesirable for AM. Commercially, zinc is considered to be the metal with the lowest melting point that can be prepared viably by water atomization.

Water atomization is similar to gas atomization in terms of the underlying mechanisms, as schematized in Figure 2.7 (Pasupathy et al. 2016). After a metal feedstock is melted in a crucible, it is transferred to a tundish with a nozzle at the bottom through which it flows downward. Water is sprayed from a high-pressure pump until the molten metal is atomized into metal droplets. The metal droplets subsequently solidify and form powder particles that are then sieved and separated. Nozzles adopted for water atomization are either multiple discrete nozzles or annular slit nozzles that are concentric with reference to the metal stream. Generally, water atomizer designs conform to a “V” configuration with a minimum of two nozzles positioned

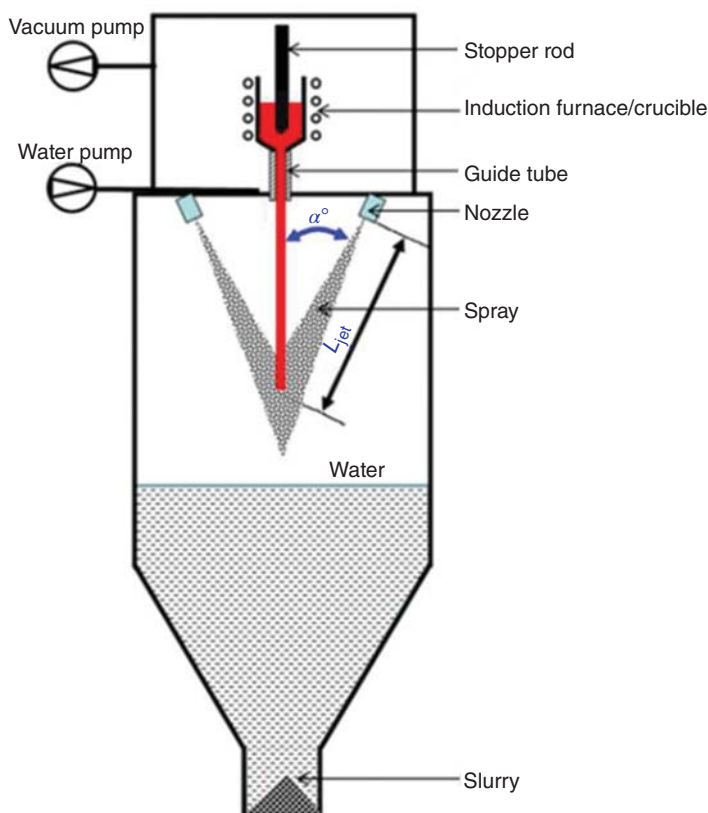


Figure 2.7 Schematic diagram of water atomization. The parameter α is the apex angle between the axis of the water jet nozzle and the molten metal stream, and L_{jet} is the length of the water jet. Source: Reproduced from Pasupathy et al. (2016)/with permission from Taylor & Francis.

symmetrically with respect to the axis of the metal stream. The free-fall configuration is adopted in common set-ups in which the molten metal exits from the bottom of the tundish and falls under gravity before colliding with the water jets.

The critical variables in water atomization include the thermophysical properties of the metal and water, geometric parameters, and process parameters. For example, thermophysical properties, such as the density and melting point of the metal, as well as the surface tension, viscosity, and degree of superheat of the molten metal, can be considered. Geometric parameters can involve the nozzle diameter, jet geometry, and the apex angle α between the axis of the water jet nozzle and the molten metal stream. Process parameters include the water pressure, water flow rate, melt flow rate, and metal stream length. The water pressure is believed to be the most effective parameter in determining the powder particle size.

Water atomization is characterized by the high density of the atomization medium (water), high cooling rate, and steam generation in the water/melt stream contact area. The high density of water results in an increase in linear momentum and kinetic energy. The steam film surrounding a metal droplet reduces the amount of heat that the droplet loses to the environment; once the film is broken, the cooling rate becomes substantially higher. The metal droplets are broken up by overheated compressed steam. The breakdown force of the steam film on a metal droplet depends on the physical conditions in the contact area, namely, the temperature and density of the steam, the water pressure, and the water flow rate.

Water atomization is primarily applied to generate powder with ferrous compositions. However, it is also employed to prepare powders from various nonferrous alloys, such as those of copper, nickel, and zinc. For example, Figure 2.8 shows a Fe–Si–B–C–P magnetic powder produced by water atomization (Liu et al. 2011). The powder exhibited both dendritic and spherical shapes because of different cooling conditions. The small Fe–Si–B–C–P droplets experienced a rapid cooling rate and solidified into irregularly shaped powder particles. In contrast, the large droplets had sufficient time to become spherical because of surface tension.

Compared to gas atomization, water atomization usually produces powder with irregular particle shapes, thereby resulting in the reduction of both the packing density and flowability of the powder. As shown in Figure 2.9a,b, gas-atomized 17-4 PH powder particles exhibited a more spherical shape and narrower particle size distribution than water-atomized 17-4 PH powder particles, which corresponded to a higher packing density and densification (Hausnerova et al. 2017). Figure 2.9c presents the torque values of both powders. A stable torque value indicates a homogeneous mixing and/or uniform dispersion of a powder within a binder that is often needed for torque measurement. The increase in torque value was marginal at lower solid loading values (up to 30 vol%) but significant at higher solid loading values. Such an increase resulted from more friction between the powder particles. The torque of the gas-atomized powder was higher than that of the water-atomized powder for small particles (sizes of 3–8 μm), while an inverse relationship could be observed for larger particles (sizes of 11–20 μm). The inverse relationship could be attributed to the irregular morphology of the water-atomized powder particles generating more friction than the gas-atomized powder particles.

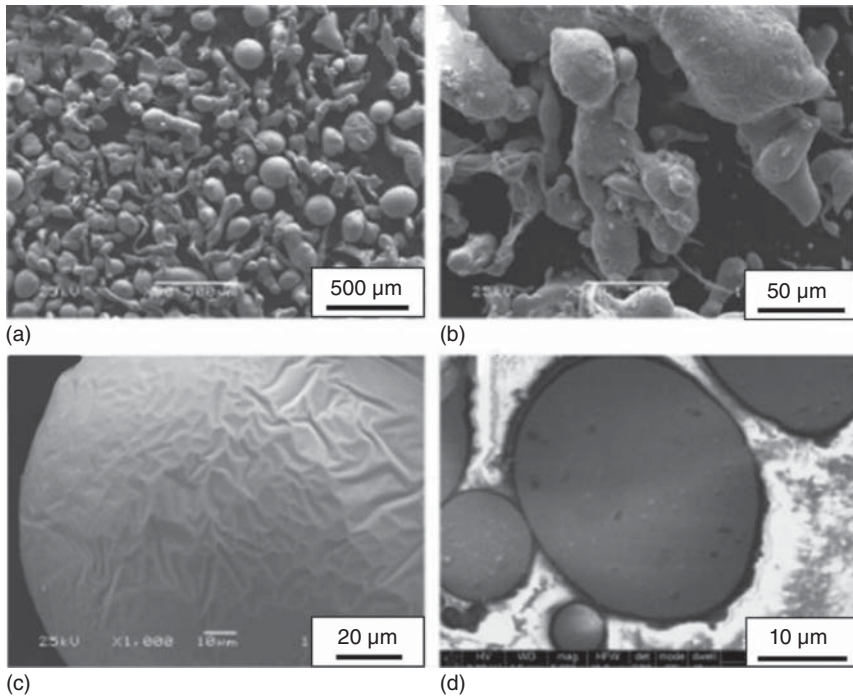


Figure 2.8 SEM images showing the morphology of Fe-Si-B-C-P magnetic powder produced by water atomization. (a) Powder particles with different shapes, (b) dendritic powder particles, (c) a spherical powder particle, and (d) the internal microstructure of the powder. Source: Liu et al. (2011)/reproduced with permission from Elsevier.

Both powders displayed pseudo-plastic behaviors with a decrease in viscosity as the shear rate increased. The temperature sensitivity of the powders could be determined from the relationship between their activation energy and the solid loading at various shear conditions. Both the gas- and water-atomized powders exhibited similar activation energies at different shear rates (Figure 2.9d).

Inconel 625 powders produced by the two atomization processes were characterized by X-ray microtomography to determine their particle size distribution, morphology, and internal porosity at high resolution (Mostafaei et al. 2018). Cross-section images of the water- and gas-atomized powder particles were obtained from X-ray microtomography scanning, which revealed their morphology and internal porosity as shown in Figure 2.10a,b. These pores were generated during the solidification stage of the atomization process. As a result, the water-atomized powder particles exhibited higher porosity and circularity indices than their gas-atomized counterparts (Figure 2.10c,d).

2.1.3 Plasma Atomization

Plasma atomization, a powder production technique jointly developed by Pyro-Genesis Inc. and Hydro-Quebec, utilizes multiple plasma arcs to atomize

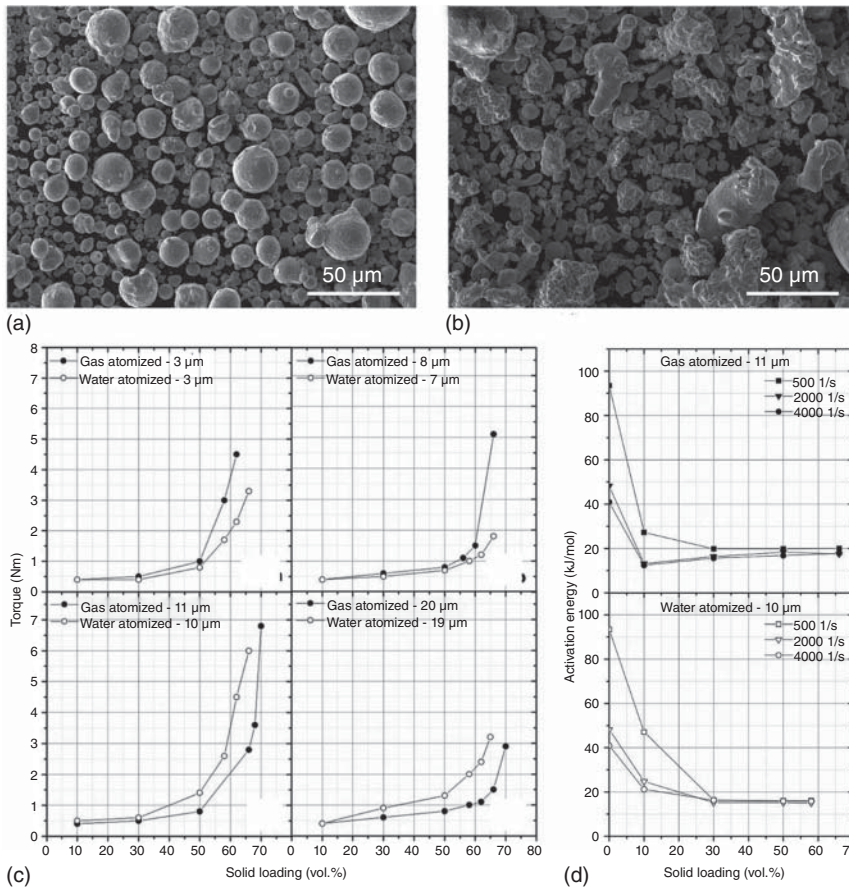


Figure 2.9 Morphology of 17-4 PH powders prepared by (a) gas atomization and (b) water atomization; (c) torque values of gas- and water-atomized powders; (d) activation energy of typical gas- and water-atomized powders produced at different shear rates. Source: Hausnerova et al. (2017)/reproduced with permission from Elsevier.

high-purity spherical powders, such as titanium, molybdenum, copper, and nickel alloy powders. Unlike high-pressure gas and water atomization, metal wires are selected as the feedstock material for plasma atomization. A schematic of the plasma atomization process is displayed in Figure 2.11 (Yolton and Froes 2015). A metal wire is fed through a hot zone created by the plasma torches, where it is melted and atomized by the plasma arc. The resultant droplets are then solidified to form spherical powder particles, with cooling rates ranging from 10^2 to 10^3 K/s.

During this process, a large amount of electrical energy is supplied to the plasma torches and converted to thermal energy, thereby generating a powerful jet of hot ionized inert gas. The high kinetic energy of the gas jet subsequently facilitates the atomization of the metal droplets. A unique feature of the plasma atomization process compared to gas atomization is that the produced powder particles are highly spherical and have almost no satellite particles attached to them (Figure 2.2b). This

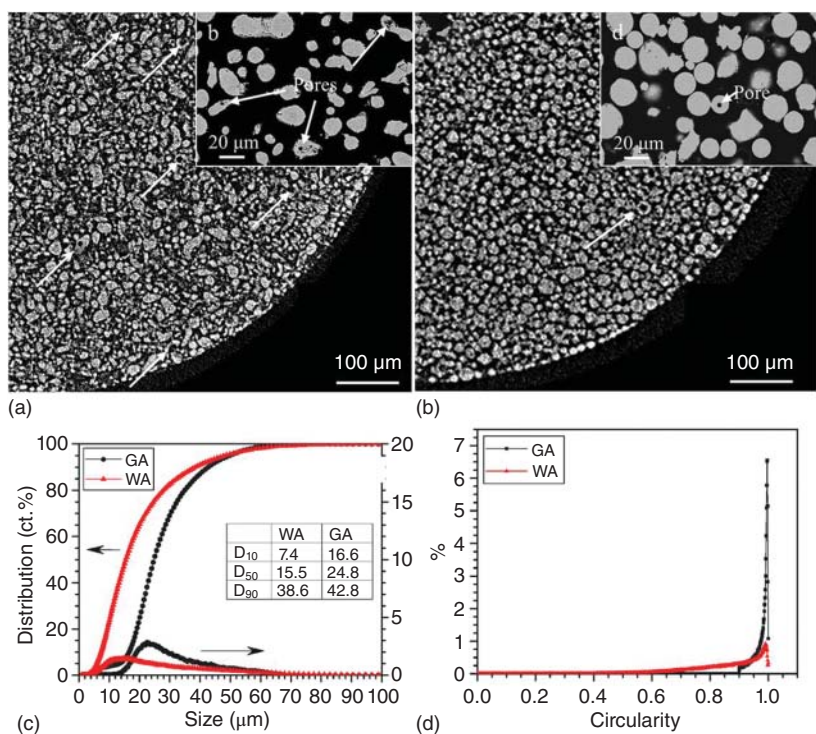


Figure 2.10 X-ray microtomography and SEM images of Inconel 625 powders prepared by (a) water atomization and (b) gas atomization; (c) particle size distribution, and (d) circularity measurements of the two powders based on Malvern Morphologi 3D data. GA, gas atomization; WA, water atomization. Source: Mostafaei et al. (2018)/reproduced with permission from Scientific Research Publishing Inc.

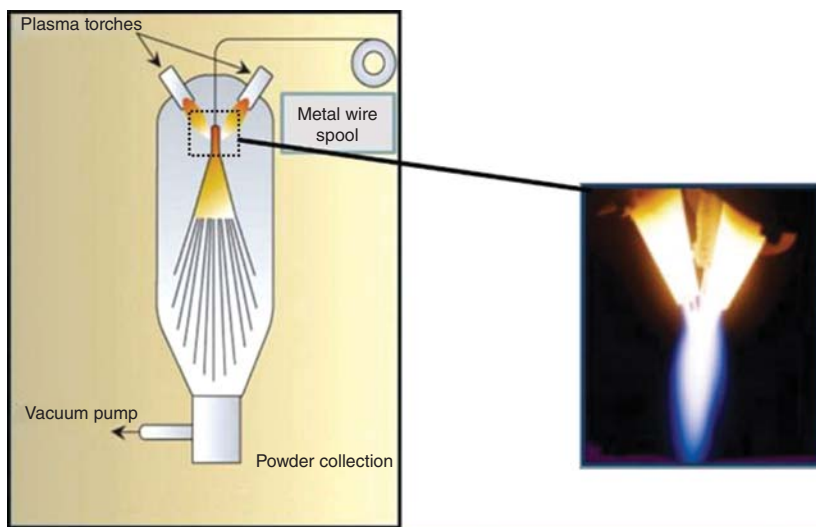


Figure 2.11 Schematic illustration of plasma atomization. Source: Yolton and Froes (2015)/reproduced with permission from Elsevier.

powder formation results from the extended hot zone generated by the plasma jets, which enables the droplets to remain in the molten state for a sufficiently long time so that powder particles with a high degree of sphericity can be obtained because of surface tension.

The particle morphology and particle size distribution of plasma-atomized powders can be influenced by the nozzle design, the velocity of the particles leaving the hot zone, and the distance across which the metal droplet solidifies. Compared to gas/water atomization, the plasma atomization process endows powders with superb characteristics for powder-based AM, such as increased flowability, higher density, and reduced porosity. The increased flowability of powders can be attributed to their relatively spherical morphology. Powders prepared by plasma atomization are also highly pure, as they have not been contaminated by any containers used to store the molten feedstock materials. Note that the feedstock material for plasma atomization can only be in the form of wires.

2.1.4 Plasma Rotating Electrode Process

The plasma rotating electrode process is a centrifugal atomization method that utilizes a rotating feedstock bar. It is a modified version of the rotating electrode process introduced in the early 1970s, in which the electric arc is substituted by plasma as the heat source. During centrifugal atomization, the molten metal flows onto the rotating disk/atomizer rotor and is sheared into a thin film at high speeds. Under the centrifugal force, the film is then flung from the edge of the disk/rotor in the form of droplets, ligaments, or sheets, depending on the rotating speed, the flow rate of the molten metal, and the atomizer rotor geometry. Gases with high thermal conductivity, such as helium, can be utilized to achieve the desired cooling rates. In addition to the rotating speed and plasma torch, another one of the key limitations of this technique is the high cost incurred, which is attributed to the enormous quantities of helium required.

A schematic of the plasma rotating electrode process is presented in Figure 2.12 (Chen et al. 2018; Sun et al. 2017a). Helium plasma is utilized to melt one end of a rapidly rotating electrode bar. The molten droplets are spun off from the surface of the rotating electrode by centrifugal forces and subsequently solidify to form flying spherical powder particles in a helium environment. Melting and atomization occur in a stainless-steel chamber at a positive gas pressure. The rotating electrodes are pre-alloyed bars that are 64 mm in diameter and are rotated at a rate of 20 000–30 000 rpm. The cooling rates are typically lower than 100 K/s, which are dependent on the gas atmosphere and the molten droplet size. The merits of the plasma rotating electrode process lie in its ability to produce highly pure and spherical powder particles.

Three spray models, namely, the direct drop formation, ligament disintegration, and film disintegration models, are illustrated in Figure 2.13 (Liu et al. 2018). A statistical equation of the actual spray model is given by

$$H = \frac{\mu^{0.17} Q \rho^{0.71} \omega^{0.6}}{\gamma^{0.88} D^{0.68}}, \quad (2.3)$$

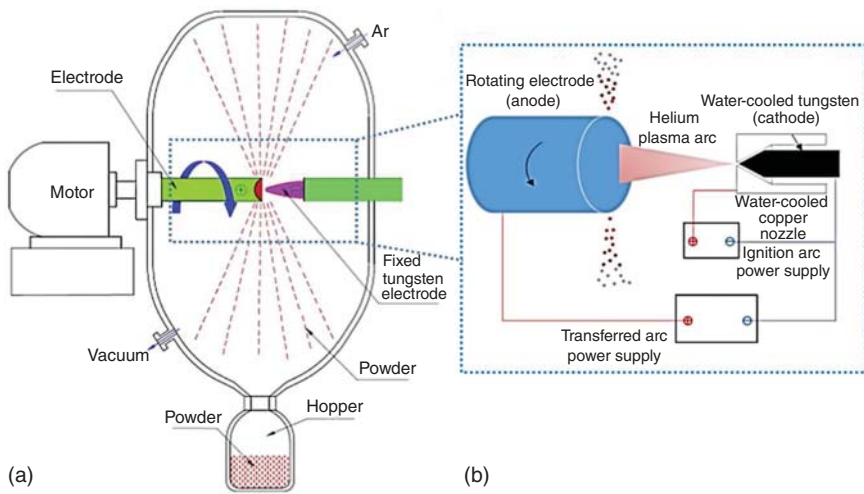


Figure 2.12 Schematic illustration of the plasma rotating electrode process. (a) Overview of the process. Source: Reproduced from Chen et al. (2018)/with permission of Elsevier. (b) Details of the process. Source: Reproduced from Sun et al. (2017a)/with permission of Springer Nature.

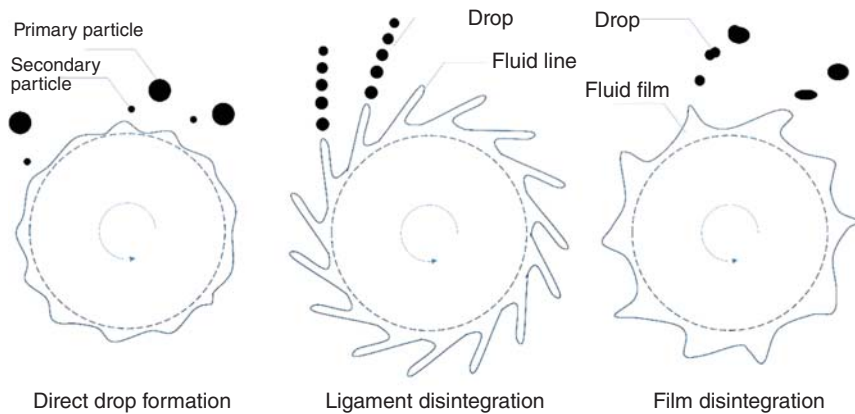


Figure 2.13 Representative centrifugal spray models of direct drop formation, ligament disintegration, and film disintegration. Source: Reproduced from Liu et al. (2018)/with permission from Elsevier.

where H is a dimensionless parameter, μ is the viscosity of the molten metal (Pa·s), Q is the melting rate of the metal (m^3/s), ρ is the density of the molten metal (kg/m^3), ω is the rotation speed of the rotor (rad/s), γ is the surface tension of the molten metal (N/m), and D is the diameter of the rotating bar (m). If H is smaller than 0.07, the main spray model is the direct drop formation model; if H is between 0.07 and 1.33, the main spray model is the ligament disintegration model; if H is greater than 1.33, the main spray model is the film disintegration model.

The plasma rotating electrode process is commonly applied to produce Fe-based, Ti-based, and Ni-based powders. Ti-6Al-4V powder particles produced by this method are spherical and possess good flow and packing features. The particle size distribution of a powder is determined by the material, electrode diameter, and rotation speed of the rotor. The average particle size D_{50} (μm) produced through the plasma rotating electrode process can be described by

$$D_{50} = \frac{K}{S\sqrt{D_e}}, \quad (2.4)$$

where K is a constant dependent on the surface tension and density of the material, S is the rotation speed (rad/s), and D_e is the electrode diameter (m). The production of fine powders can be boosted by increasing S and D_e . However, larger D_e and higher S values correspond to a higher accuracy requirement for the electrode dimensions to minimize out-of-balance forces. In addition, an increase in the melting rate leads to a remarkable rise in the yield of fine powders (e.g. with a size range below $45 \mu\text{m}$).

Powders with different particle size distributions exhibit different levels of surface oxidation. Spherical pre-alloyed Nb-Si powders with particle size distributions of 45–75, 75–180, 180–250, and 250–380 μm were produced through the plasma rotating electrode process (Guo et al. 2017). An oxygen-enriched layer with a thickness of 5.14 nm was formed on the surface of the pre-alloyed powders. The oxygen content was discovered to decrease exponentially with the etching depth. Meanwhile, the external surface of the Nb-Si powder was Nb-depleted and (Ti, Si)-enriched, which could be attributed to the low thermodynamic stability of Nb_2O_5 .

Figure 2.14 displays the morphology and particle size of Ti-6Al-4V powders produced by gas atomization, the plasma rotating electrode process, and plasma atomization (Chen et al. 2018). Compared to the Ti-6Al-4V powder particles prepared by gas atomization and plasma atomization, the powder prepared by the plasma rotating electrode process possessed a low argon content and porosity. Additionally, the powder prepared by gas atomization yielded more satellite particles than those produced by the plasma rotating electrode process and plasma atomization (for further details, refer to Section 2.1.1).

The particle size plays a vital role in determining the morphology and porosity of the atomized powder (Figure 2.14g,h). Powders produced by the plasma rotating electrode process possess fewer gas pores than gas-atomized and plasma-atomized powders because the molten droplets in the former process are formed by centrifugal forces instead of high-pressure gases. Moreover, large powder particles usually possess a higher gas content than small particles. This phenomenon can be attributed to the following two factors: first, during gas and plasma atomization processes, large droplets disintegrate into several small droplets that are concomitant with the breaking up of gas bubbles. Thus, no gas pores are formed. As a corollary, small powder particles possess fewer gas pores than large ones.

Second, during the plasma rotating electrode process, the surface tension of the original droplets from the electrode is lower than that of other droplets in flight. Consequently, the large original droplets can easily capture the surrounding argon gas. In comparison, the small droplets in flight undergo a high cooling rate, which

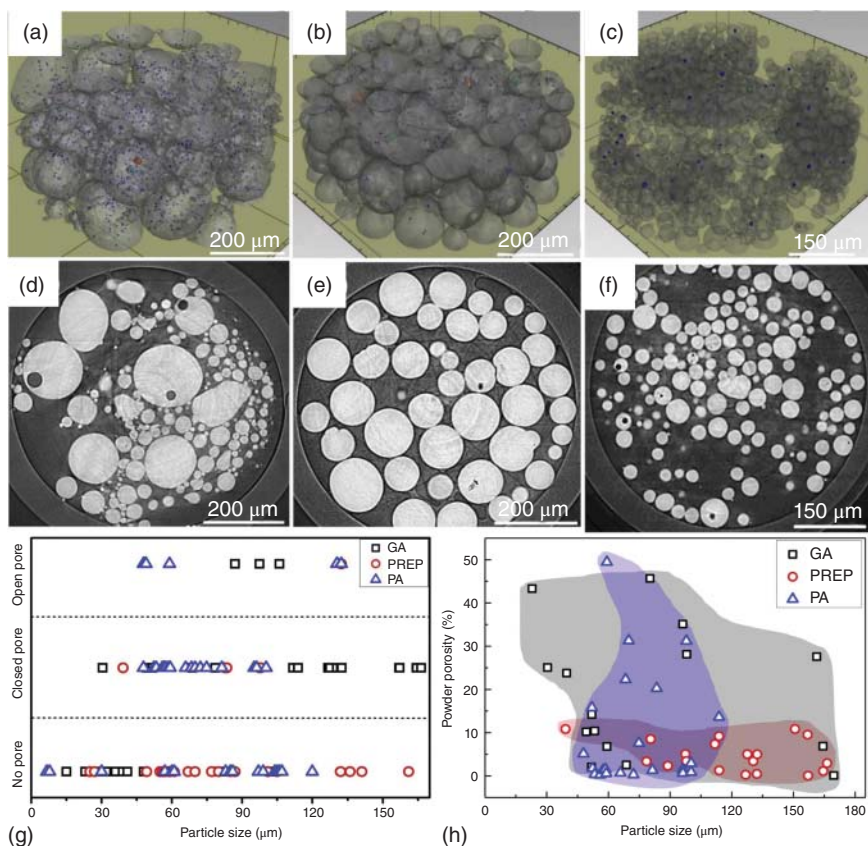


Figure 2.14 Morphology of Ti-6Al-4V powders produced by different atomization processes. (a–c) Computed tomography (CT) analysis showing the 3D reconstructed models of the powder from gas atomization, the plasma rotating electrode process, and plasma atomization, respectively, and (d–f) SEM images showing the cross-sectional morphology of the powders from the three processes, respectively. The particle size of the powders: (g) relationship between the particle size and pore characteristics; (h) statistic of porosity with respect to the particle size. GA, gas atomization; PA, plasma atomization; PREP, plasma rotating electrode process. Source: Chen et al. (2018)/reproduced with permission from Elsevier.

results in a higher surface tension and a lower capacity to entrap gases. Table 2.3 compares the properties of different powders prepared by the plasma rotating electrode process and gas atomization.

2.2 Mechanical Mixing

Mechanical mixing is another widespread method to produce metal powders for AM. Based on the principles of the solid-state mixing process, raw materials are converted into powder by external mechanical forces. Mechanical mixing processes for metal powder production can be divided into two categories, namely,

Table 2.3 Comparison of the plasma rotating electrode process and gas atomization for different powders.

Powder	Characteristics	Plasma rotating electrode process	Gas atomization
Ti-6Al-4V ^{a)}	Powder volume (mm ³)	2.329	3.877
	Pores volume (mm ³)	0.000399	0.002117
	Porosity (%)	0.017	0.055
	Average diameter (μm)	72	94
Ti-6Al-4V ^{b)}	Flowability (s/50g)	29.6	33.5
	Apparent density (g/cm ³)	2.59	2.38
	Average particle size (μm)	105	70
	Argon gas content (μg/g)	0.16	0.77
Ni718 ^{c)}	Porosity (%)	0.08	0.20
	Powder flow rate (kg/h)	2.21	2.02
	Average dendrite spacing (μm)	5.0	3.8
	Laves phase (wt%)	15.82	12.46
TiAl ^{d)}	γ matrix (wt%)	2.51	5.82
	Dendritic microstructure (%)	52	0
	Rosette microstructure (%)	28	100
	Featureless microstructure (%)	20	0

a) (Ahsan et al. 2011);

b) (Chen et al. 2018);

c) (Zhong et al. 2016);

d) (Fuchs and Hayden 1992).

mechanical alloying and mechanical blending (Suryanarayana 2001). The main difference between them is that material transfer involves mechanical alloying but not mechanical blending. Table 2.4 summarizes the typical metal composite powders prepared through mechanical alloying and mechanical blending. Table 2.5 lists the advantages and disadvantages of the two processes.

Mechanical alloying is a high-energy milling process for producing fine metal composite powders with tailored microstructures (Arami and Simchi 2007; Krasnowski and Kulik 2008; Suryanarayana 2001). As schematized in Figure 2.15 (Han et al. 2020b), the process begins with mixing different powders in a specific ratio. Subsequently, the powder mixture is loaded into a grinding bowl containing the grinding medium (generally steel balls). The main part of this method involves fracturing and cold welding a mixture of metallic or nonmetallic powders in a highly activated ball milling process. When the powder particles are trapped between the colliding grinding balls, the materials experience large plastic strain under extreme hydrostatic compression, which results in their fracture. As the process continues, fracturing and welding repeatedly occur, which results in the successive refinement of the powder particles.

Table 2.4 Comparison of mechanical alloying and mechanical blending for the powder preparation of metal matrix composites in powder-based AM.

Process	Composite powder	Particle size
Mechanical alloying with high energy	SiC/Fe ^{a)}	Fe: 20 μm ; SiC: 27 μm
	TiC/316L ^{b)}	316L: 45 μm ; TiC: 50 nm/1 μm
	Al ₂ O ₃ /Al ^{c)}	Al: 17 μm ; Al ₂ O ₃ : 10 nm
	TiC/Al–Si10–Mg ^{d)}	Al–Si10–Mg: 30 μm ; TiC: 50 nm
	TiC/Ti ^{e)}	Ti: 23 μm ; TiC: 50 nm
	TiB/Ti ^{f)}	Ti: 49 μm ; TiB ₂ : 3.5–6 μm
	TiC/TiAl ^{g)}	Ti: 30 μm ; Al: 16 μm ; Graphite: 30 μm
	TiB ₂ /TiAl ^{h)}	TiAl: 28 μm ; TiB ₂ : 3–5 μm
	MoTiAl/Al ₂ O ₃ /CNT ⁱ⁾	MoTiAl: 1–45 μm ; Al ₂ O ₃ : 140 nm; CNT: 2–15 nm
Mechanical blending with low energy	HA/316L ^{j)}	316L: 28 μm ; HA: <100 nm
	WC/Fe ^{k)}	Fe: 5–30 μm ; WC: 5–15 μm
	WC/Ni718 ^{l)}	Ni718: 15–45 μm ; WC: 25–45 μm
	TiB ₂ /Ni625 ^{m)}	Ni625: 11–45 μm ; TiB ₂ : 5–12 μm
	SiC/Al12Si ⁿ⁾	Al12Si: 20–63 μm ; SiC: 11–45 μm
	TiB ₂ /Al–Si10–Mg ^{o)}	Al–Si10–Mg: 19.3–74.8 μm ; TiB ₂ : 2–5 μm /58 nm
	TiB ₂ /Ti–6Al–4V ^{p)}	Ti–6Al–4V: 20–70 μm ; TiB ₂ : 2.71 μm
	B ₄ C/Ti ^{q)}	Ti: 16–59 μm ; B ₄ C: 500 nm
	HA/Ti ^{r)}	Ti: 30.8 μm ; HA: 50 nm

a) Song et al. (2014);

b) AlMangour and Grzesiak (2016);

c) Han et al. (2016);

d) Gu et al. (2015);

e) Gu et al. (2012);

f) Attar et al. (2014);

g) Gu et al. (2009);

h) Li et al. (2017);

i) Zhou et al. (2018b);

j) Wei et al. (2015);

k) Gu et al. (2018);

l) Rong and Gu (2016);

m) Zhang et al. (2016);

n) Li et al. (2016);

o) Aversa et al. (2017);

p) Cai et al. (2019);

q) Han et al. (2020);

r) Han et al. (2018).

Table 2.5 Summary of the advantages and disadvantages of mechanical alloying and mechanical blending.

Process	Advantages	Disadvantages
Mechanical alloying with high energy	● Fast and simplified ● Decent dispersion of reinforcements	● Particle deformation ● Uncertainty in tailoring the powder particle size ● Poor powder flowability ● Introduction of undesirable phases and contamination
Mechanical blending with low energy	● Fast and simplified ● Nearly retains the shape, particle size, and distribution of the powder ● Decent powder flowability	● Poor dispersion for nano-sized powder particles ● Limited to the preparation of alloy powders

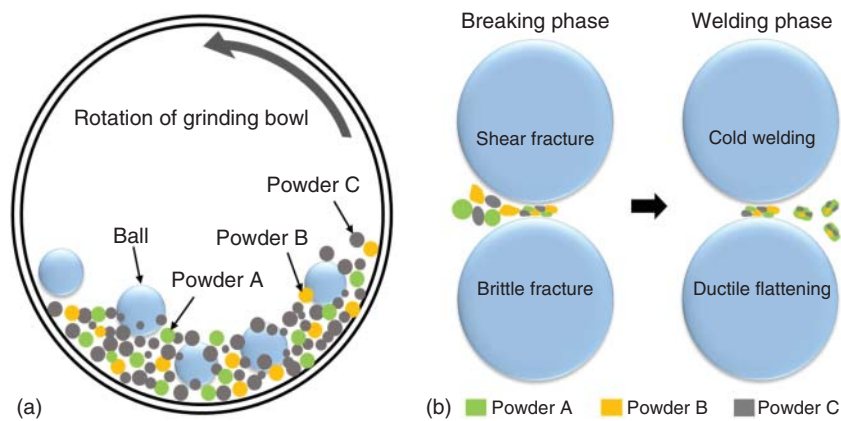


Figure 2.15 Schematic of mechanical alloying. (a) Process, and (b) mechanism. Source: Reproduced from Han et al. (2020)/with permission from John Wiley & sons.

Shaker milling, planetary ball milling, and attritor milling are typical high-energy milling techniques for mechanical alloying (Neikov et al. 2009). Shaker milling is the most commonly utilized technique for laboratory experiments and alloy screening, in which 0.2–20 g of powder is milled at a time. A typical setup for shaker milling comprises a vial containing grinding balls and powders. The vial is fixed by a clamp that swings back and forth several thousand times per minute. The materials used for the vials are stainless steel, hardened steel, zirconia, and alumina. The standard machine model is the SPEX mill, which is manufactured by SPEX CertiPrep.

Planetary ball milling can process a few hundred grams of powder at a time. In contrast to shaker milling, the vials are installed on a rotating support disk and

rotated about their axes. The centrifugal forces produced by the vials and the supporting disk are opposite to one another because of their opposite rotating directions. As a result, friction and impact effects are induced, and they act on the powder and grinding balls in the vials. The materials used for the vials and grinding balls include chrome steel, chromium–nickel steel, agate, silicon nitride, sintered corundum, zirconia, tungsten carbide, and plastic polyamide. The energy transferred during planetary ball milling is lower than that during SPEX milling due to the lower impact frequency in the former technique.

An attritor mill consists of a vertical drum with a series of impellers. By setting the impellers at right angles to one another, they activate the ball charge, thereby reducing the powder particle size. Such size reduction is derived from the impact between (i) the grinding balls, (ii) the grinding balls and the container wall, and (iii) the grinding balls, the agitator shaft, and the impellers. As a result, large quantities of powder (about 0.5–40 kg) can be processed in one milling cycle. In addition, the speed of the grinding media in attritor mills is lower than in SPEX mills, and thus the energy transferred during attritor milling is relatively low.

In mechanical alloying, the required microstructure of the powder can be achieved through an optimal configuration of different factors, such as the type of milling technique, milling container, milling speed, milling time, milling temperature, milling atmosphere, grinding medium, ball-to-powder weight ratio, extent of vial filling, and process control agent (Suryanarayana 2001). For example, the morphology of mechanically alloyed Al6061–TiO₂ nanocomposite powders was determined to change with the milling duration, and a rise in milling time corresponds to a decrease in particle size (Figure 2.16a–f) (Sivasankaran et al. 2010).

A schematic describing the formation of nanocomposite powders during mechanical alloying is shown in Figure 2.16g. It consists of six stages: (i) the preparation of micro-sized (colored) and nano-sized (black) powder particles; (ii) the deformation and flattening of the micro-sized powder particles, fragmentation of the nano-sized powder particles, and adherence of the nano-sized powder particles to the surface of the micro-sized powder particles; (iii) cold-welding predominance; (iv) the formation of equiaxed powder particles; (v) random welding orientation and the formation of necks; and (vi) attaining equilibrium among breaking-up, cold welding, and fracturing.

At the initial stage of milling, the apparent density of powders decreases continuously and reaches a minimum value after 10 hours. Then, it begins to increase with the milling time until a plateau is reached. This change in the apparent density is attributed to the cold welding of powder particles during the initial milling stage and the fracturing of powder particles during the later stages. The apparent density first reduces and then increases because of the fragmentation and morphological variations of the powder particles, which are both induced by cold welding.

Mechanical alloying applies to a wide range of pure metals and alloys, particularly refractory metal materials. It is also useful for developing new materials, such as metal matrix composites, HEAs, metallic glasses, and intermetallic compounds. For example, the milling time is crucial in determining the phase composition, grain size, and lattice strain of HEA powder particles. Increasing the milling time weakens

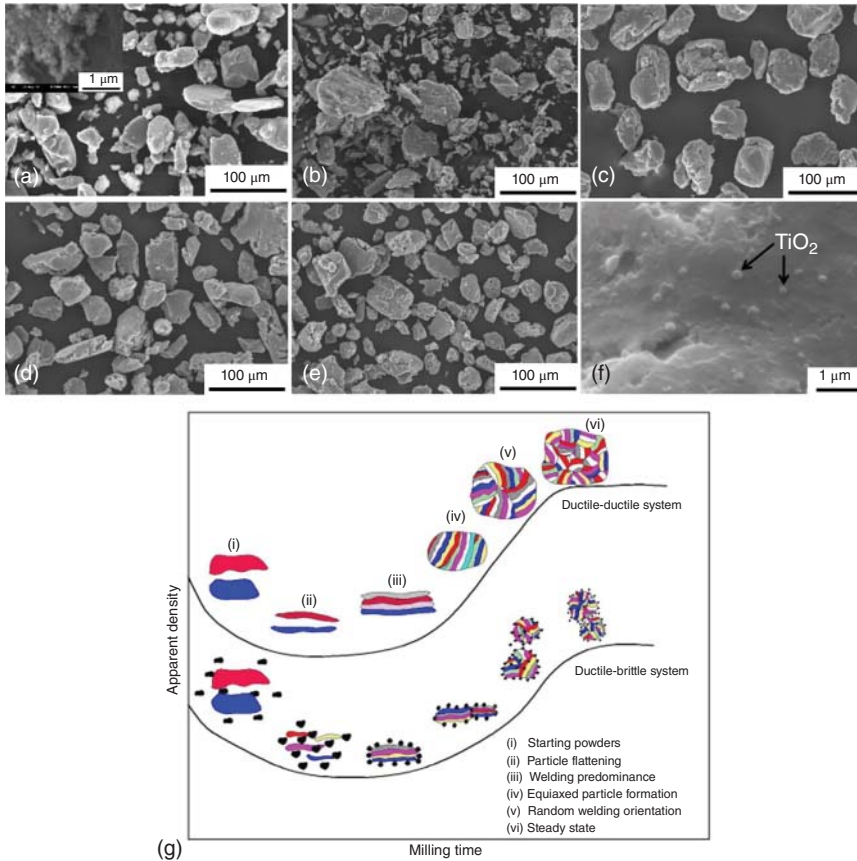


Figure 2.16 SEM images displaying the morphology of Al6061-TiO₂ composite powders with different milling durations. (a) 1 hour, (b) 5 hours, (c) 10 hours, (d) 20 hours, and (e) 40 hours, in which (f) is the enlarged image of (e). (g) Schematic illustration of the relationship between the milling time, morphology, and apparent density of different types of powders. Source: Sivasankaran et al. (2010)/reproduced with permission from Elsevier.

the diffraction peaks of Al_{0.4}CoFeNiSi_{0.4} powder (Zhang et al. 2018), thereby posing difficulty in identifying the phase composition of HEA powders. A prolonged milling time also reduces the grain size and increases the lattice strain within the powder particles because of the increased grain boundary fraction and lattice deformation. Additionally, the repetition of fracturing and welding during the process accelerates the formation of solid-solution phases. Consequently, elements with low melting points or brittle crystal structures are dissolved preferentially.

In addition, due to the intensive impaction of the powder particles, mechanical alloying allows powders of nano sizes and multiple phases (e.g. metastable crystalline phases, quasi-crystalline phases, and supersaturated solid phases) to be achieved. However, the powder particles usually exhibit irregular shapes, which are detrimental to their flowability for AM. This problem can be resolved by

employing the plasma spheroidization technique to endow the powder particles with a spherical shape for better printability (see Section 2.4.1 for further details).

Mechanical blending requires lower energy and a shorter time than mechanical alloying for powder preparation. Additionally, material transfer hardly occurs when blending powders with different shapes. Therefore, mechanical blending becomes increasingly preferable for preparing metal matrix composite powders. However, due to their high aspect ratio, dispersing nanoparticles via mechanical blending is problematic because the nanoparticles can agglomerate under strong van der Waals forces. For example, Figure 2.17 shows the powder mixture of titanium and hydroxyapatite prepared by mechanical blending, whereby titanium powder particles are covered with hydroxyapatite nanoparticles (Han et al. 2017). The agglomeration of the nano-hydroxyapatite powder occurs because of its high surface activity, which increases in severity with the nano-hydroxyapatite content.

A critical drawback of mechanical alloying and mechanical blending is that impurities are included in the powder during milling. Such contamination can alter the chemical composition and stability of the powder products. The impurities may originate from chemical impurities within the feedstock powder, the milling equipment, or the environment. The use of process control agents may also lead to powder contamination. Moreover, the surface area of small powder particles is typically sufficiently large to facilitate such contamination.

Powder contamination in mechanical alloying and mechanical blending can be reduced by using: (i) the same material as the powder for the mill container and the grinding medium, (ii) materials for the grinding medium and the mill container that are harder and stronger than the powder, and (iii) an inert gaseous atmosphere for the milling process.

2.3 Reduction Process

Reducing metal oxides and metallic salts is one of the most common methods of producing metal powders. Using ores and industrial metallurgical waste as raw materials is an economically viable strategy. The advantages of the reduction process include a simple operation procedure, easy control of technological parameters, high production efficiency, and low cost, thereby rendering it suitable for the industrial production of metal powders. Below, four typical reduction processes are introduced, namely, the hydride–dehydride process, oxide reduction, chloride reduction, and carbonyl reactions.

2.3.1 Hydride–Dehydride Process

Unlike the atomization processes, the hydride–dehydride process includes crushing, milling, and screening to process larger blocks of metal feedstock into finer powder particles without melting them. Such a technique is particularly suitable for producing powders of materials that are brittle when exposed to hydrogen gas, such as titanium, zirconium, vanadium, and tantalum. The hydride–dehydride process is

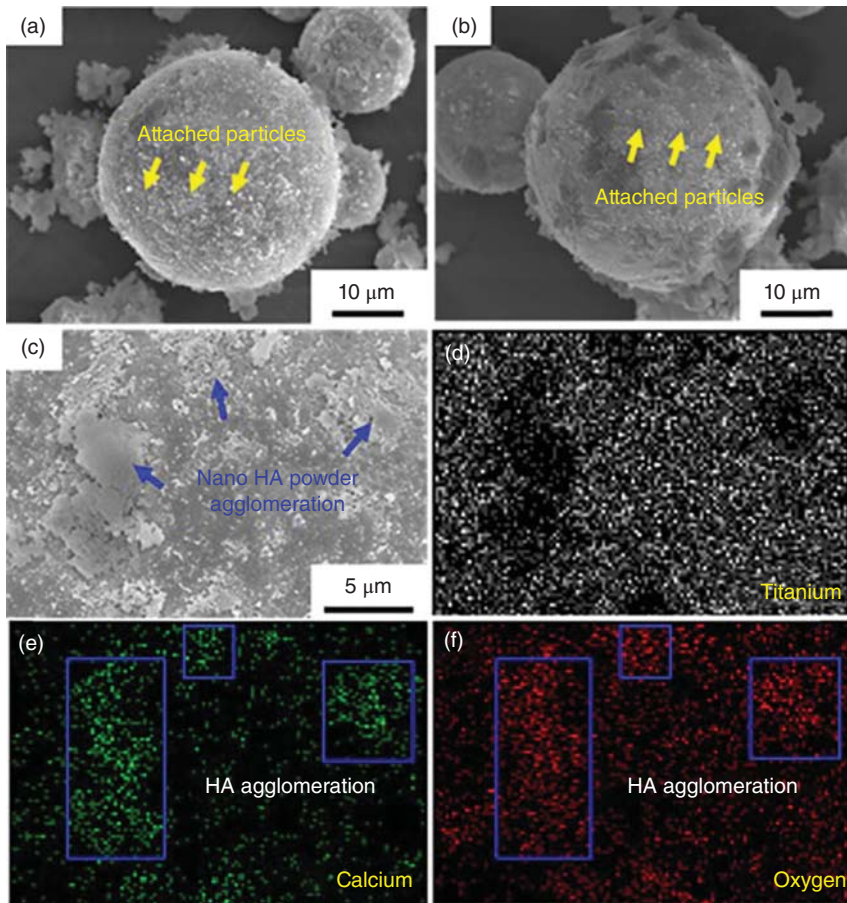


Figure 2.17 SEM micrographs of mechanically blended powders. (a) Titanium–2 wt% hydroxyapatite, (b) titanium–5 wt% hydroxyapatite, and (c) the surface of a titanium–5 wt% hydroxyapatite powder particle. (d–f) EDS mapping of the powder particle showing Ti, Ca, and O, respectively. Source: Han et al. (2017)/reproduced with permission from Elsevier.

most adopted for synthesizing powders of titanium and its alloys, such as commercially pure titanium and Ti–6Al–4V. A schematic of the hydride–dehydride process for obtaining titanium or Ti–6Al–4V powder is illustrated in Figure 2.18 (Agripa and Botef 2019). Titanium or Ti–6Al–4V hydrides are first produced in a hydride unit filled with hydrogen gas through heating at a high temperature of 300–700 °C. The hydrogenated titanium blocks are crushed, milled, and sieved to produce the powder. Subsequently, the powder is returned to the hydride unit for the dehydride process, where it is reheated within a high vacuum environment at about 350 °C to remove any excess hydrogen (McCracken et al. 2011). After the hydride–dehydride process, the titanium or Ti–6Al–4V powder becomes very brittle and can be ground into fine powder particles. Mechanical crushing in ball mills with screening procedures enables the manufacturing of powder with specific particle sizes.

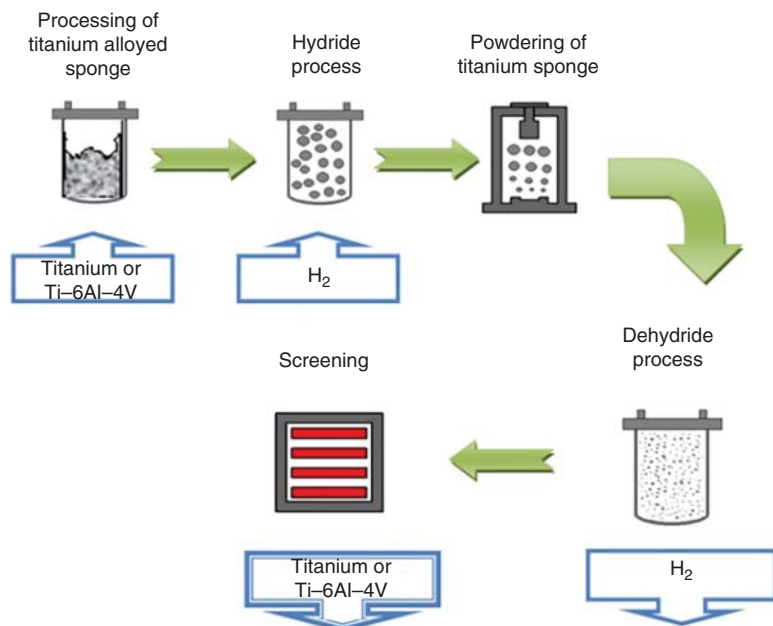


Figure 2.18 Schematic of the hydride–dehydride process in producing titanium or Ti–6Al–4V powder. Source: Agripa and Botef (2019)/IntechOpen/CC BY-3.0.

The hydride–dehydride process is a feasible approach for tailoring the particle size and chemical composition of powders for different requirements and applications. In addition, compared to the atomization processes, the hydride–dehydride process is a simple procedure with low cost and energy consumption, and it can be utilized for large-scale powder production. However, the disadvantages associated with this process include the underlying challenges of hydrogen purification and the high reactivity of titanium toward the residual hydrogen, which results in fragile final products. Table 2.6 compares titanium powders prepared by the hydride–dehydride and plasma rotating electrode processes (Lou et al. 2015). The powder particles of the former approach exhibit a smaller size, lower density, higher oxygen content, and more irregular shapes than the latter.

Table 2.6 Comparison of titanium powders prepared by the hydride–dehydride and plasma rotating electrode processes.

Process	Oxygen content (wt%)	D_{10} (μm)	D_{50} (μm)	D_{90} (μm)	Apparent density (g/cm^3)	Tap density (g/cm^3)
Hydride–dehydride	0.33	20.84	47.69	91.03	1.42	2.08
Plasma rotating electrode process	0.09	107.24	153.48	218.67	2.74	2.95

Source: Reproduced from Lou et al. (2015)/with the permission of Springer Nature.

The oxidation of hydride–dehydrided powders may occur due to the raw materials and the hydride–dehydride process. The oxygen content in powder particles primarily depends on the specific surface area of the powder. Once a powder is exposed to air, the large specific surface area instantly causes the powder to oxidize, and thus a high oxygen content is obtained. For hydride–dehydrided titanium powder, a Ti–O passivation layer could be induced in the form of TiO_2 , Ti_2O_3 , and TiO , where the oxygen content in the oxide layer could reach up to 23.1 wt% (Zhang et al. 2021). When the Ti–O layer was produced on the powder surface, the oxygen content could not decrease unless the passivation layer was deoxidized by certain reductants (e.g. calcium vapor).

Titanium powder produced by the hydride–dehydride process is usually modified to obtain a cost-effective powder with good flowability. For example, hydride–dehydrided titanium powder was modified by the ball milling process (Xu et al. 2019). The powder was milled for two to six hours using a planetary ball milling machine, and the production efficiency of the powder was found to be 65–70%. As shown in Figure 2.19a, the powder particles exhibited irregular shapes and sharp edges before milling, but they became near-spherical with sharp edges after two hours of milling (Figure 2.19b). When the milling time was increased to four hours, the powder particles were near-spherical with no apparent angularity (Figure 2.19c). However, the powder particles became flatter after six hours (Figure 2.19d). The average particle size of the modified powder was found to be about 30 μm after ball milling and sieving. As the milling time was extended, the apparent density and tap density of the powder increased from 1.26 to 1.64 g/cm^3 and from 1.88 to 2.10 g/cm^3 , respectively.

The hydride–dehydride process also allows for the preparation of metal matrix composite powders. For example, a Ti/TiC composite powder could be prepared by directly introducing TiH_2 and TiC powders to pure titanium powder during the dehydride process (Peillon et al. 2015). The TiH_2 powder played a vital role in controlling the powder particle size. Moreover, the hydride–dehydride process is the most common approach for preparing powders containing Ti, Zr, and Hf elements. Zr–Ti–Nb foams with different levels of Nb content were fabricated from powders produced by the hydride–dehydride process. Such foams exhibited excellent biocompatibility with subcutaneous and bone tissues (Maya et al. 2012).

Apart from the standard hydride–dehydride process, a hydride–milling–dehydride system has been developed to produce zirconium powder (Figure 2.20a) (Kelley and McDeavitt 2013). The design of this process was based on the requirement to dehydride zirconium hydride at a temperature of 1000 °C. Figure 2.20b,c show the morphologies of the powder particles under different milling times. It was demonstrated that an increase in the milling time reduced the average powder particle size and improved the uniformity of the powder particle size.

2.3.2 Oxide Reduction

The oxide reduction process can be conducted to prepare pure metal powders, such as iron, cobalt, copper, and tungsten, through the reduction reactions of metal oxide ores by gaseous hydrogen, carbon monoxide, or dissociated ammonia. It is a simple

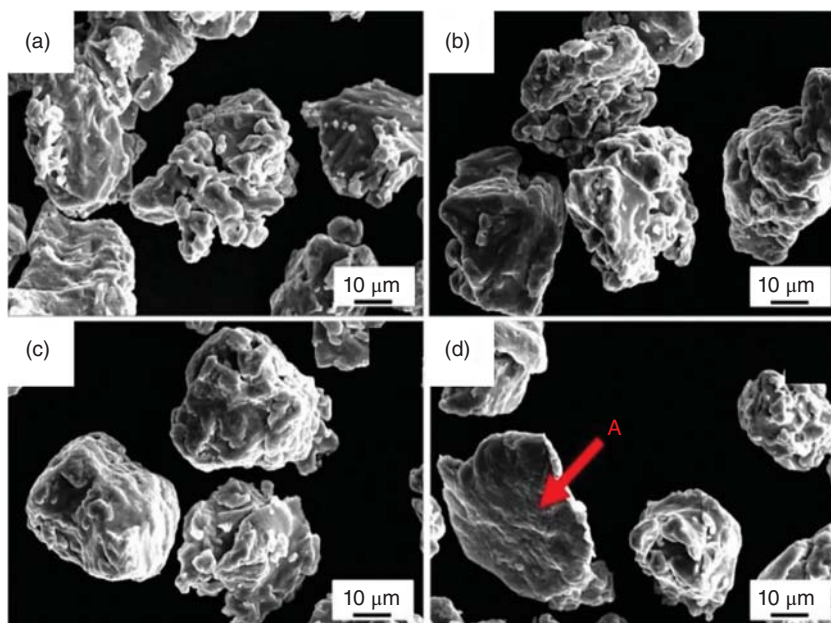


Figure 2.19 SEM images displaying the morphology of hydride–dehydrided titanium powders produced after various milling durations. (a) 0 hour, (b) 2 hours, (c) 4 hours, and (d) 6 hours. The symbol “A” indicates a relatively flat surface. Source: Xu et al. (2019)/reproduced with permission from Elsevier.

process that produces powders with a well-controlled particle size distribution, good formability, and high sinterability by treating the oxide ores and tailoring the reduction atmosphere and milling time.

The reduction reactions for metal oxides can be described by the following equations:



where M denotes the metal element. Equation (2.6) describes an indirect carbothermic reduction at low temperatures, and Equation (2.7) represents a direct carbothermic reduction at high temperatures.

The electrolysis process consists of key components such as an electrolyte, a power supply, and electrodes. Metal elements are deposited on the cathode of an electrolytic cell in the form of powder through the electrolysis of the electrolyte, which is an aqueous salt solution. The composition and viscosity of the electrolyte, current density, and temperature will affect the deposition process. The merits of the process are the high purity of the powder produced, good control over the powder particle size, and the ability to produce ultrafine powder. However, the high power consumption

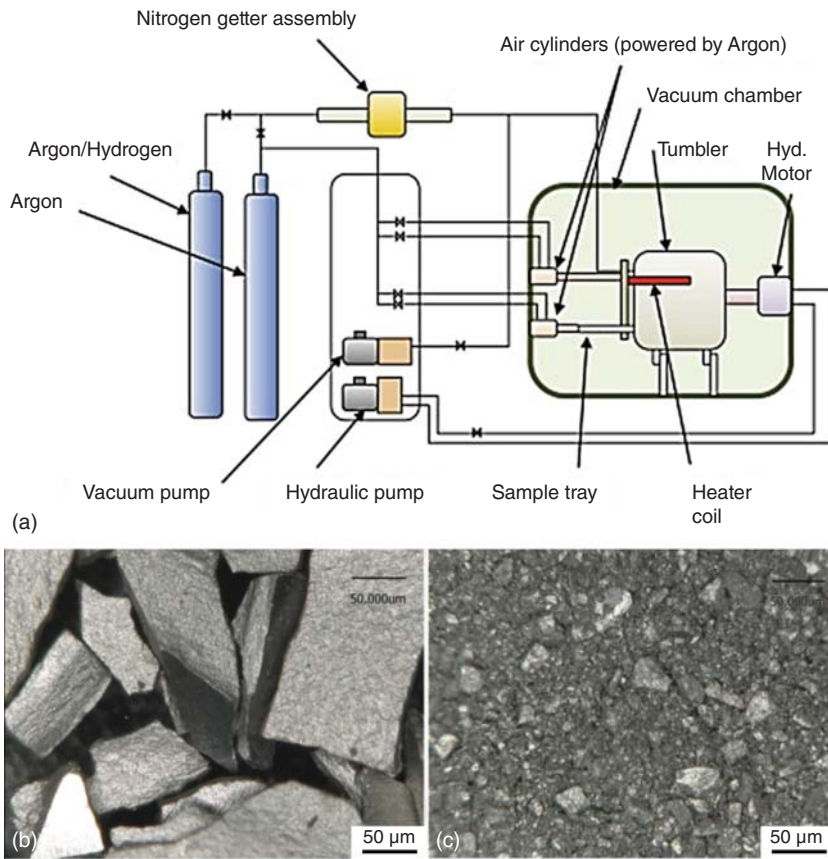


Figure 2.20 (a) Schematic of a hydride-milling-dehydride system. Resultant morphology of zirconium powder after milling for (b) 45 minutes and (c) 24 hours. Source: Kelley and McDeavitt (2013)/reproduced with permission from Elsevier.

of this process corresponds to high cost, and thus it is not widely employed in powder production.

A novel electrolytic technique, named the Fray-Farthing-Chan Cambridge process, has been developed to produce low-cost titanium powder with high purity (Fray et al. 2009). This process utilizes molten salt electrolysis to extract metals from their oxides. Figure 2.21 shows a graphical representation of the process. The titanium oxide acts as a cathode, and graphite acts as an anode. The two electrodes are immersed in a molten salt bath at a temperature of 800–1000 °C. Then, oxide ions depart from the titanium oxide cathode and are carried across the molten salt to the anode, where they react to form carbon dioxide and carbon monoxide. Once the carbon dioxide and carbon monoxide bubbles have dispersed, pure titanium is retained. This novel extraction technique can be applied to produce spherical titanium powder for AM.

Oxides, chlorides, and zirconates are commonly employed in the electrolysis process. The main requirements for electrolytes include: (i) the exclusion of metal

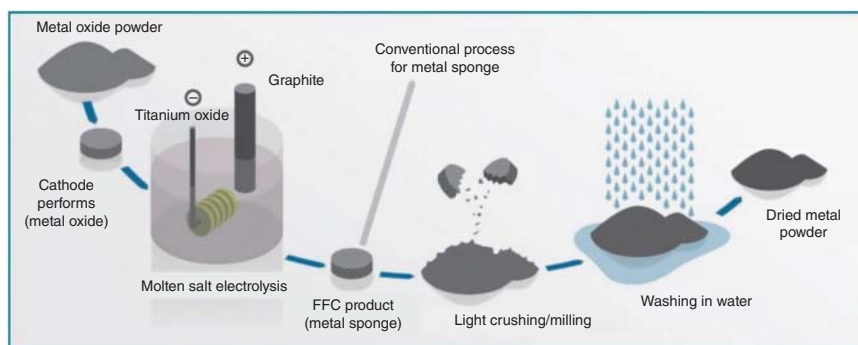


Figure 2.21 Schematic illustration of the Fray–Farthing–Chan Cambridge electrolysis process. FFC, Fray–Farthing–Chan Cambridge electrolysis process. Source: Reproduced from Fray et al. (2009)/with permission from Elsevier.

impurities that possess a higher positive electrode potential than the metal being electrolyzed; (ii) high solubility of the electrolyte with the metal being electrolyzed; (iii) low viscosity and high fluidity of the electrolyte at the temperature of the electrolysis process, which is advantageous for the discharge of the anodic gas and the uniformity of the electrolyte composition; (iv) a low melting point of the electrolyte to reduce the required electrolytic temperature; (v) high conductivity of the molten electrolyte; and (vi) high chemical stability of the electrolyte in both solid and liquid states.

The electrolysis process has been applied to produce copper, chromium, and manganese powders. In such cases, a dense and brittle deposit is produced, which is subsequently crushed to form powder particles. The electrolysis process is capable of yielding high-purity powders with controllable sizes. However, it is limited to producing pure metal powders, as the production of alloyed powders may require additional measures, such as washing, drying, reducing, annealing, and crushing of the powders.

2.3.3 Chloride Reduction

The chloride reduction process is employed to produce metal powders by thermally decomposing metal chlorides. The TiROTM process, a relatively new method developed by CSIRO for producing pure titanium powder, is introduced herein (Doblin et al. 2012). This cost-effective process produces pure titanium in a continuous fluidized bed in which TiCl_4 reacts with magnesium powder. The process flow diagram can be divided into two stages. The first stage involves the chemical reactions between TiCl_4 and magnesium powder particles in a fluidized bed to produce small titanium metal powder particles, which are homogeneously dispersed with spheroidal MgCl_2 powder particles. Overall, TiCl_4 reacts with magnesium and is thermally reduced to a solid MgCl_2/Ti composite in the fluidized bed reactor. The fluidized bed reactor employs argon as a sweeping gas to feed liquid TiCl_4 and magnesium powder to the bed.

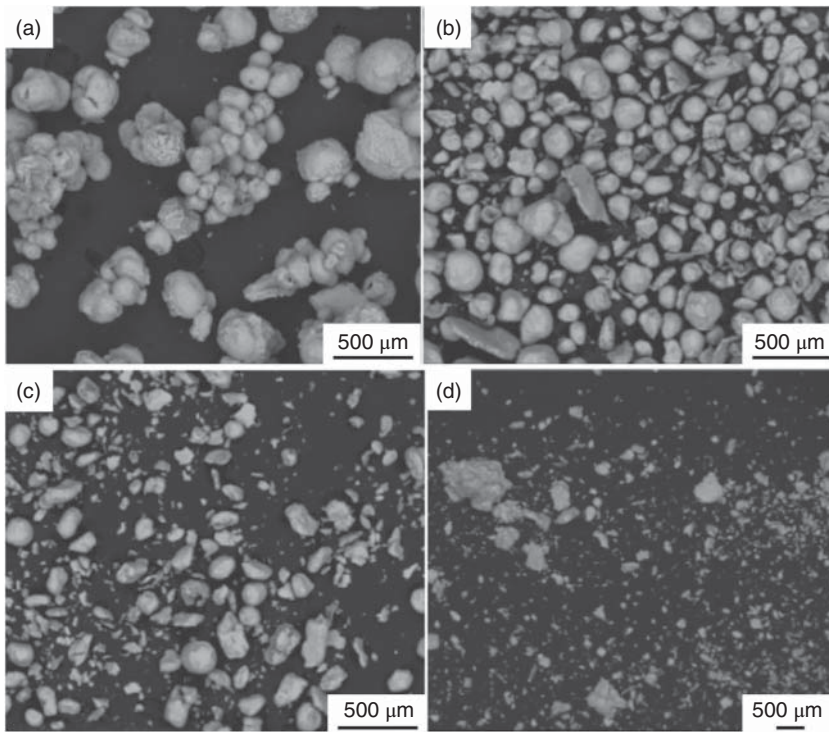


Figure 2.22 SEM images showing the morphology of titanium powder produced by the TiRO™ process after different milling times. (a) 0 minutes, (b) 0.5 minutes, (c) 2 minutes, and (d) 10 minutes. Source: Doblin et al. (2013)/reproduced with permission from Trans Tech Publications Ltd.

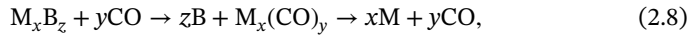
The second stage includes a vacuum distillation process in which high-purity titanium powder is separated from the MgCl_2/Ti composite. The vacuum-distilled powder is then grounded and screened, and titanium powder particles up to a maximum size of 125 mm are selected. The process has low energy consumption, high powder yield, and low labor requirements. As a result, the TiRO™ process can produce titanium powder that meets commercially pure titanium grade 3 standards.

However, the as-prepared titanium powder particles after vacuum distillation are still too large to be used for powder bed fusion AM. Fortunately, a high-shear milling process can reduce the powder particle size (Doblin et al. 2013). After milling for 0.5 minutes, the powder particles were more densely packed, and some powder particles were observed to deform into platelets. In addition, with an increase in milling time, the number of smaller powder particles increased while more powder particles were flattened (Figure 2.22). However, a long milling time may be disadvantageous because the agglomeration of powder particles may occur.

2.3.4 Carbonyl Reactions

The carbonyl reaction is extensively utilized for chemical deposition. It involves the high-pressure and high-temperature treatment of metals by carbon monoxide,

which produces metal carbonyls. The metal carbonyls then undergo thermal decomposition to produce the metal powders and recycle the carbon monoxide. The process can be described by the following reaction:



in which M and B represent the metal and ballast (e.g. oxygen, salt residue, and impurities), respectively; x , y , and z refer to the coefficients that depend on the metal species; and $M_x(CO)_y$ is the carbonyl of the metal M.

The carbonyl reaction is a popular chemical process for producing nickel and iron powders. It can produce micro- and nano-sized powders because the thermal decomposition of a metal carbonyl refines its constituent metal. In such a process, nickel reacts with carbon monoxide and forms gaseous nickel carbonyl ($Ni(CO)_4$), which can be decomposed back into refined nickel metal at a moderate temperature with the recovery of the carbon monoxide. Fine nickel powder can then be prepared through thermal shock decomposition. Meanwhile, iron carbonyl from iron powder/scrap can be thermally decomposed to prepare spherical iron powder with an average particle size of 10 μm (Antony and Reddy 2003), which is the ideal material for fabricating chemical power supply plates and can also be employed as catalysts. However, additional efforts are still required to determine the applicability of carbonyl-derived powders for metal powder-based AM.

2.4 Powder Modification

In addition to the commonly used powder preparation processes introduced in Sections 2.1–2.3, there are preparation processes aimed at modifying metal powders to have a high degree of sphericity, such as plasma spheroidization, granulation–sintering–deoxygenation, and fluidized-bed granulation. In particular, the plasma spheroidization process has been increasingly applied to produce spherical metal powders for powder-based AM.

2.4.1 Plasma Spheroidization

Plasma spheroidization is one of the new advanced techniques developed for producing metal powders for AM. This technique allows powder particles to be reshaped into the ideal spherical shape, and the resultant powder particles usually exhibit comparable sphericity to gas-atomized powder particles. Therefore, it is extremely suitable for treating nonspherical and irregular powders with low contamination under high temperatures (3000–10 000 K) and rapid quenching rates (about 10^6 K/s). Plasma spheroidization can effectively produce high-purity powders with high degrees of sphericity and small particle sizes. In addition to the ability to alter the particle shape, plasma spheroidization also reduces the internal porosity of a powder, enhances its flowability and purity, and increases its apparent density. Most importantly, this process can be conducted during the post-treatment of recycled AM powders.

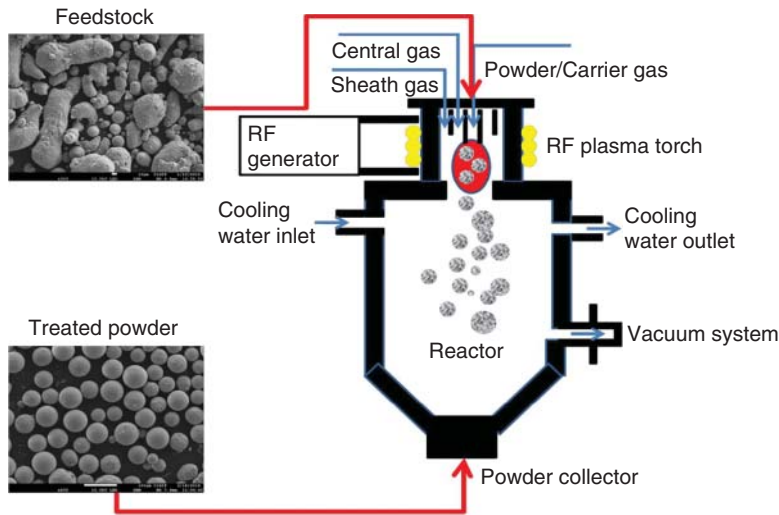


Figure 2.23 Schematic illustration of induction plasma spheroidization. RF stands for radio frequency. Source: Wang et al. (2017)/reproduced with permission from Elsevier.

Nevertheless, preparing fine spherical alloy powder with low oxygen content in a cost-effective manner still poses a great challenge for plasma spheroidization. The level of impurity in the spheroidized powder mainly depends on the feedstock. Another potential issue is the rapid evaporation of alloying elements with low melting points at plasma temperatures. Generally, the plasma spheroidization process is not utilized in large-scale powder production due to its low productivity and high cost.

As schematically illustrated in Figure 2.23, the plasma device primarily consists of plasma generating, powder feeding, and powder collecting systems, reactor and cooling chambers, and a cyclone separator (Wang et al. 2017). An induction plasma torch is formed via an electromagnetic coupling of the input electrical energy and the discharge gas medium. An oscillating magnetic field is formed by an alternating current of radio frequency range passing through a suitable coil. This magnetic field redirects an ionized gas load flowing within the discharge cavity, which provides ohmic heating to maintain the plasma temperature. Based on this principle, gases (such as argon) are purged and ionized to generate a high-temperature plasma torch. While passing through the plasma torch, the irregularly shaped powder particles are melted to form metal droplets. These droplets finally form spherical powder particles through rapid solidification.

The plasma spheroidization process includes four stages. The first stage is the pre-treatment of raw powder. A vacuum drying cabinet is utilized to reduce moisture within the raw powder. The dried powder is then sieved to optimize the particle size distribution. The second stage is the generation of plasma after the system is purified via air evacuation and argon gas purging. The third stage is the spheroidization of the pretreated raw powder, which is fed into the plasma reactor chamber. When the powder passes through the high-temperature zone, it is completely melted and forms

Table 2.7 Processing parameters of plasma spheroidization for different metal powders.

Powder	Center gas flow rate (l/min)	Sheath gas flow rate (l/min)	Carrier gas flow rate (l/min)	Reactor pressure (kPa)	Plasma power (kW)	Powder feed rate (g/min)
Ta ^{a)}	30	85	4	95	60	50
Nb-based alloy ^{b)}	—	—	—	—	15	30
W ^{c)}	20–30	85–115	3.5	14.7	15	4–25
W ^{d)}	15	55	5.5	14.7	40	25
TiAl ^{e)}	—	85	—	—	45	—

a) Qin et al. (2019);

b) Goncharov et al. (2019);

c) Zi et al. (2018);

d) Wang et al. (2017);

e) Tong et al. (2015).

spherical droplets. The dispersing gas converts these droplets into smaller droplets, which are then cooled and solidified to form regular spherical powder particles. Finally, the spheroidized powder is gathered by the powder collector.

Plasma spheroidization applies to many materials, such as titanium-based, aluminum-based, and niobium-based alloys, pure titanium, and pure tungsten. Feedstock materials used in plasma spheroidization can be powders produced by the hydride–dehydride process, the electrolysis process, or any other process that produces irregularly shaped powder particles. Table 2.7 lists the processing parameters of plasma spheroidization for different metal powders.

As one of the most critical processing parameters, the powder feed rate influences the heat absorption and the duration for which the powder particles remain in the flame area. The latter effect is crucial because the powder particles cannot be melted outside the high-temperature area. The influence of the powder feed rate on the morphology and size distribution of tungsten powder particles produced by plasma spheroidization was investigated (Figure 2.24a) (Zi et al. 2018). Once the feed rate was lowered to 15–20 g/min, a small number of spherical powder particles were produced (Figure 2.24b,c). Most tungsten powder particles were spherical when the feed rate was below 15 g/min (Figure 2.24d–f). When the feed rate was below 10 g/min, powder particle aggregation was limited, and the spheroidization efficiency of the tungsten powder exceeded 95%. Moreover, the particle size distribution curve of the tungsten powder spheroidized at feed rates below 10 g/min was narrower than the distribution curves of raw powders and the spheroidized powders at higher feed rates. As a result, some aggregated powder particles could not maintain their original morphology under surface tension and ultimately split into smaller spherical powder particles. A decrease in the feed rate increased the spheroidization efficiency of the tungsten powder particles but reduced their particle size.

Figure 2.25 presents the property analysis of raw and spheroidized tungsten powders (Wang et al. 2017). After spheroidization, both the basic flow energy (BFE) and

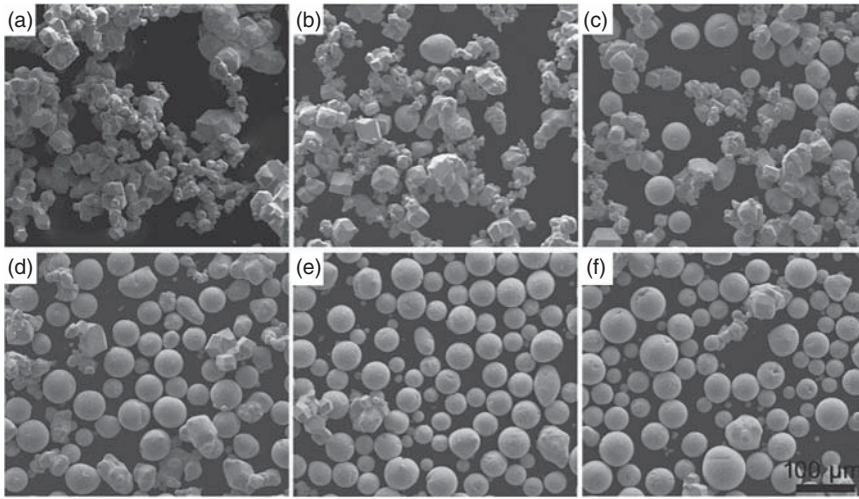


Figure 2.24 SEM images showing the morphology of tungsten powder before and after plasma spheroidization. (a) Raw powder, and (b–f) spheroidized powder produced at feed rates of 25, 15, 10, 6, and 4 g/min, respectively. Source: Zi et al. (2018)/reproduced with permission from Taylor & Francis.

the specific energy (SE) of the powder were significantly reduced (Figure 2.25a). Larger BFE and SE implied strong cohesion of the powder. The aerated flow energy (AE) of the spheroidized tungsten powder was lower than that of the raw powder, as shown in Figure 2.25b. A low AE indicated low cohesive strength among the powder particles and resulted in higher flow performance. The compressibility of these two powders is shown in Figure 2.25c. The compressibility percentage of the spherical powder was larger than that of the raw powder. The delivery of powder with high compressibility is relatively unaffected by non-cohesive powder particles with a low viscosity. A remarkable distinction in permeability could be observed between the raw and spheroidized powders (Figure 2.25d). A lower pressure drop resulted in higher powder permeability. Larger gaps were presented among the spherical powder particles than among the raw powder particles, which provided a way for air to escape from the powder container.

Recently, spherical NbMoTaW refractory HEA powders were prepared by spray drying and plasma spheroidization (Liu et al. 2021). They exhibited a homogeneous particle size distribution in the range of 10–60 µm and a BCC phase. In addition, the powders achieved an ultrahigh microhardness of over 10 GPa, which is 50% higher than their bulk counterparts. This new process for preparing spherical refractory HEA powders holds great potential for applications in metal powder-based AM.

2.4.2 Granulation–Sintering–Deoxygenation

Recently, a novel approach, granulation–sintering–deoxygenation, has been developed to prepare low-cost spherical titanium powder for AM. As its name suggests,

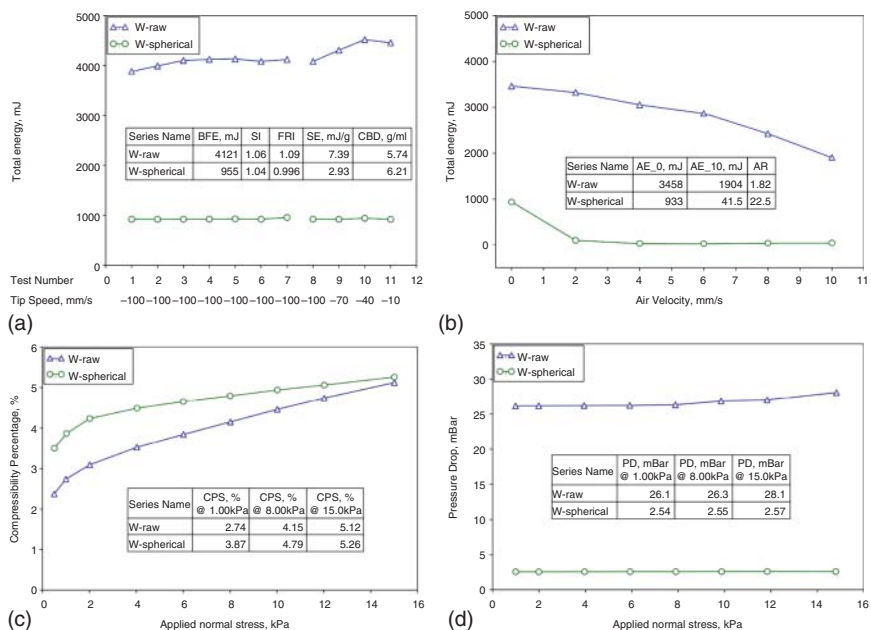


Figure 2.25 Property analysis of raw and spheroidized tungsten powders. (a) Basic flow, (b) aeration, (c) compressibility, and (d) permeability. Source: Reproduced from Wang et al. (2017)/with permission from Elsevier.

the granulation–sintering–deoxygenation process combines the underlying mechanisms of a few popular low-cost processes to prepare powders, such as granulation, sintering, and deoxygenation.

In granulation–sintering–deoxygenation, low-cost scrap titanium hydride powder blended with other pure metal powders can be selected as the raw material. During the granulation process, titanium hydrides containing other alloying elements are milled into fine powder particles and subsequently granulated via spray-drying to form spherical granules with the required sizes. Then, the spherical granules are sintered to produce high-density titanium alloy particles. In the deoxygenation process, the pre-densified spherical titanium alloy powder is deoxygenated to meet the industry standard of oxygen concentration. Overall, the granulation–sintering–deoxygenation process consumes less energy than atomization methods.

Figure 2.26 shows a schematic illustration of a typical granulation–sintering–deoxygenation process for producing Ti–6Al–4V powder (Sun et al. 2016). In the study, Ti–6Al–4V hydride powder with a maximum particle size of 74 μm , produced from Ti–6Al–4V scrap by cleaning, hydrogenation, milling, and sizing, was used as the raw material. The powder was milled in a solvent to reduce its particle size down to 10 μm (Figure 2.27a). Afterward, the slurry was delivered to a spray dryer filled with argon gas to produce spherical granules comprising fine Ti–6Al–4V hydride powder particles, which were then sieved for post-processing.

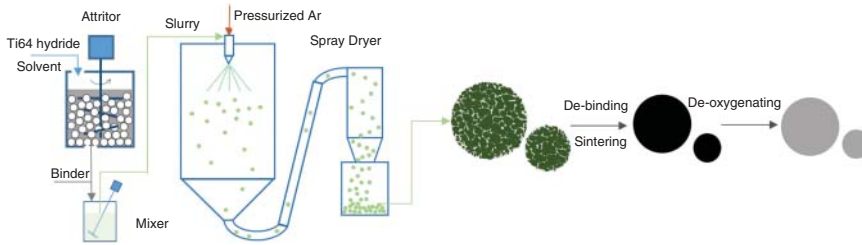


Figure 2.26 Schematic illustration of the granulation-sintering-deoxygenation process for the production of spherical Ti-6Al-4V powder. Source: Reproduced from Sun et al. (2016)/with permission from Elsevier.

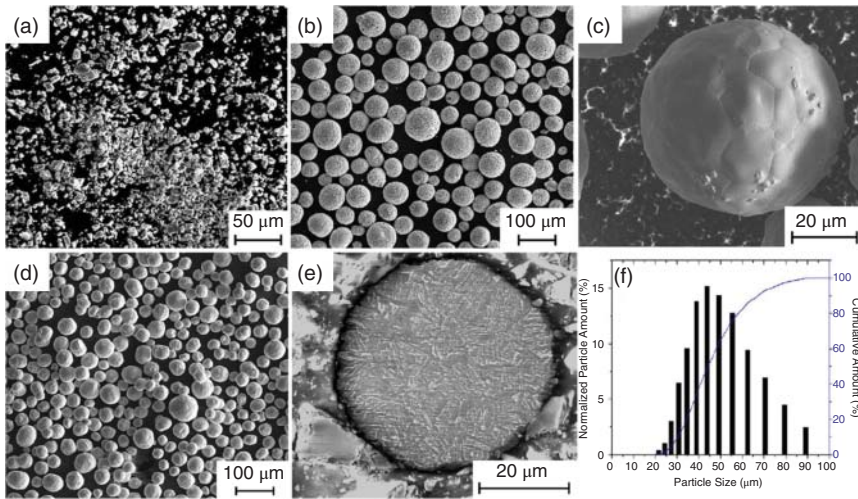


Figure 2.27 SEM images showing the morphology of Ti-6Al-4V powder particles produced during the granulation-sintering-deoxygenation process. (a) As-milled hydrogenated scrap powder, (b) spray-dried powder, (c) a sintered spherical powder particle, (d) spherical powder after deoxygenation, and (e) cross-sectional view of a deoxygenated powder particle. (f) Powder particle size distribution after deoxygenation. Source: Sun et al. (2016)/reproduced with permission from Elsevier.

The spherical granules were thermally de-bounded at a temperature between 200 and 400 °C and then sintered in a furnace filled with argon gas. A calcium oxide separator was utilized in the debinding and sintering processes to prevent sintering amongst the granules. After sintering, the calcium oxide separator was leached by dilute hydrochloric acid (HCl) and washed with water. The sintered Ti-6Al-4V powder was then deoxygenated using calcium metal at a temperature of 750 °C for 12 hours in a tube furnace filled with flowing argon gas. The spray-dried and sintered granules, as well as the deoxygenated powder particles, were found to exhibit a high degree of sphericity (Figure 2.27b-d). The spray drying parameters can be optimized to increase the yield of powder particles with specific sizes to fulfill certain requirements in various applications.

Cross-sectional SEM images of the final deoxygenated powder particles reveal that they were densified and exhibited a lamellar structure (Figure 2.27e), and their sizes ranged from 20 to 90 μm (Figure 2.27f). The resultant powder possessed a flowability of 27.5 s/50 g, an apparent density of 2.34 g/cm³, a tap density of 2.78 g/cm³, and a true density of 99.5%. This powder has been successfully processed by laser powder bed fusion, and the tensile properties of the printed parts were comparable to those of mill-annealed Ti-6Al-4V parts (Sun et al. 2017b).

The surfaces of powder particles prepared by granulation–sintering–deoxygenation are not as smooth as those prepared by gas atomization, plasma atomization, and the plasma rotating electrode process. However, it is a common practice to reuse spherical titanium powder after printing, and thus the surface of its particles will become rougher after several printing cycles. The surface quality of powders produced via the granulation–sintering–deoxygenation approach can be comparable to that of recycled Ti-6Al-4V powder produced by atomization, which indicates that the powder prepared by granulation–sintering–deoxygenation can fulfill the surface quality requirements for metal powder-based AM.

2.4.3 Fluidized-bed Granulation

A novel fluidized bed technique has been developed to modify titanium powder for AM (Ding et al. 2019). This study used a fluidized bed reactor to treat titanium powder produced by the hydride–dehydride process, as schematized in Figure 2.28a. The powder was first treated in a fluidized bed reactor at different temperatures of 400–500 °C. During the high-temperature fluidizing process, collision, friction, and drag forces were present among the powder particles. The high temperature reduced the yield strength of the titanium powder so that the drag forces could grind the surface of the powder particles and reduce their bulges. Therefore, the morphology, surface roughness, and particle size distribution of the powder particles can be modified to improve the flowability of the powder.

The extent of shape modification by such a technique depends on the treatment temperature, time, gas flow rate, and powder particle size. As shown in Figure 2.28b, the average powder particle size increased marginally with a treatment temperature of up to 550 °C. Therefore, treatment by the fluidized bed technique influenced the powder particle size marginally. The flowability of the powder after the treatment was measured to be 35.2 s/50 g, which was similar to that of the most commonly utilized AM powders (Figure 2.28c). The modified surface morphology of the resultant powder particles (Figure 2.28a) reduced the frequency of multiple-point interactions, which was attributed to their improved smoothness and decreasing number of small powder particles. Such an effect decreased the surface friction among the powder particles, thereby leading to a smoother powder flow. However, increasing the treatment temperature to 600 °C adversely affected the powder flowability (Figure 2.28c), which was a result of minor sintering occurring among individual powder particles at treatment temperatures exceeding 500 °C.

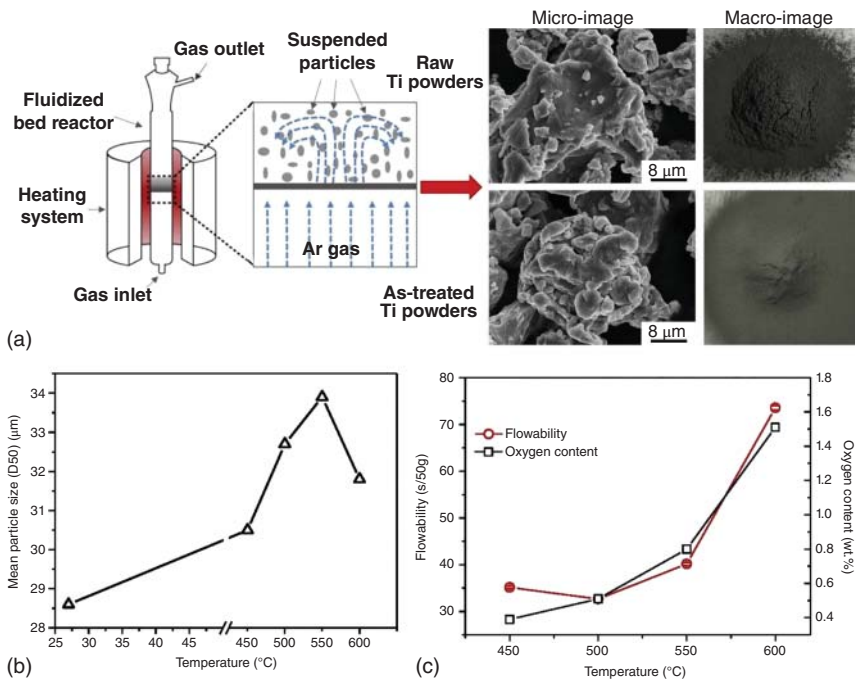


Figure 2.28 (a) Schematic illustration of the fluidized-bed treating process for titanium powder produced by the hydride–dehydride process and the powder morphology before and after treatment, (b) average powder particle size as a function of temperature, and (c) powder flowability and oxygen content as functions of temperature. Source: Ding et al. (2019)/reproduced with permission from Elsevier.

2.5 Summary

This chapter presents the fundamentals and characteristics of the preparation processes of metal powders for AM. Determining the desired properties of an AM powder is a critical step in selecting a suitable powder preparation process to enable the printing of high-quality parts for industrial applications. Representative AM metal powders developed by the various preparation processes are summarized in Table 2.8. Currently, atomization processes are the most popular class of methods for producing a variety of metal powders. Most metal powders used in powder-based AM are prepared by gas atomization. However, additional research is required to understand the powder properties important for ensuring the repeatable manufacturing of metal parts.

The preparation processes used by representative commercial companies for powder production are presented in Table 2.9. Many industrial companies have focused on developing atomization methodologies and ensuring process stability to produce metal powders for AM purposes. Most companies are devoted to the development of metal powders through gas atomization.

Table 2.8 Summary of representative AM metal powders developed by various preparation processes.

	Representative powder													
Process	Fe-based	Ti-based	Ni-based	Al-based	Cu-based	Nb-based	Co-based	Mg-based	Zr-Based	TiAl	Cemented carbide	Refractory metal	HEA	Metallic glass
Gas atomization	✓	✓	✓	✓	✓		✓	✓		✓	✓	✓	✓	✓
Water atomization	✓		✓	✓	✓		✓						✓	✓
Plasma atomization		✓			✓		✓							
Plasma rotating electrode process	✓	✓	✓			✓	✓		✓	✓			✓	
Mechanical mixing	✓	✓	✓	✓	✓	✓	✓	✓		✓	✓	✓	✓	
Hydride–dehydride		✓							✓			✓		
Oxide reduction	✓		✓		✓	✓	✓	✓	✓					
Chloride reduction	✓	✓												
Electrolysis process	✓	✓	✓		✓	✓			✓					
Carbonyl reaction	✓		✓				✓							
Plasma spherodization		✓	✓	✓		✓	✓			✓	✓	✓		

Table 2.9 The preparation processes used by representative commercial companies for powder production.

Process	Representative commercial companies
Gas atomization	ATI Powder Metals (USA), Crucible Materials Corp (USA), Iowa Powder Atomization Technologies (USA), Puris LLC (USA), Ametek specialty metal products (USA), Carpenter Technology Corp (USA), ALD Vacuum Technologies GmbH (Germany), TLS Technik (Germany), Affinity International (China), Osaka Titanium Technologies (Japan), H.C. Starck GmbH (Germany), Höganäs Sweden AB (Sweden), Sandvik Materials Technology (Sweden), LPW Technology Ltd (UK)
Water atomization	H.C.Starck GmbH (Germany), Höganäs Sweden AB (Sweden), LPW Technology Ltd (UK)
Plasma atomization	AP&C (Canada), LPW Technology Ltd (UK), ARCAM AB (Sweden)
Plasma rotating electrode process	Timet (USA), LPW Technology Ltd (UK), Phelly Materials (China), Baoji Orchid Ti (China)
Hydride–dehydride	Affinity International (China), Teledyne Wah Chang (USA), Global Titanium (USA), Ametek specialty metal products (USA), Osaka Titanium Technologies (Japan)
Chloride reduction	CSIRO (Australia)
Plasma spheroidization	Tekna Plasma Systems (Canada), Global Advanced Metals (USA)

Metal powder preparation techniques have existed for decades. Before the advent of metal AM techniques, high costs and a lack of industrial demand are the main reasons behind the unremarkable development of new powder preparation processes. The wide application of AM techniques in various industries significantly stimulates the supply and demand market for metal powders, which provides great opportunities for developing novel powder preparation processes in the future.

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3

Laser Powder Bed Fusion

In recent years, laser powder bed fusion (LPBF) has gained the most attention from academia and industry among metal powder-based additive manufacturing (AM) techniques. The small laser spot size and powder particle size in LPBF enable the high-precision printing of metal parts. In addition, the ultrahigh cooling rates result in refined microstructures, contributing to the excellent mechanical performance of the printed parts. This chapter discusses the history, fundamentals, process characteristics, powder materials, and equipment of LPBF, as well as microstructure and mechanical properties of LPBF-printed parts, including mechanical metamaterials.

3.1 History

LPBF utilizes high-energy laser beams to melt metal powders. The patent for LPBF was first filed to the German Patent and Trade Mark Office in 1997 by F & S Stereolithographietechnik GmbH with Fraunhofer ILT and later published in 1998 (Meiners et al. 1998). The ASTM International F42 standards committee initially classified selective laser melting (SLM) under the category of laser sintering, but it was later rectified as the two processes are fundamentally different. Both SLM and laser sintering are now grouped under powder bed fusion (PBF). Another name for LPBF is direct metal laser sintering (DMLS), as dictated by the EOS company. The first test systems of DMLS were developed by EOS and installed in 1994. The first commercial EOSINT M 250 system was established in 1995, enabling complex and massive parts to be built with high accuracy and good surface quality.

LPBF rapidly became a commercial success after the advent of the EOSINT M 250 system, and the development of the materials and process advanced rapidly because of the EOS–ERD cooperation. In 1997, an improved version of the system was introduced, which allowed the part to be built with a 50 μm layer thickness, thus significantly enhancing the surface quality by reducing the stairstep effect. A significant milestone in part quality improvement was achieved in 2001 with the introduction of DirectSteel 20, a steel powder that can be printed with a layer thickness of only 20 μm . The same layer thickness was also achieved in 2002 for the bronze-based DirectMetal 20 powder.

In 2004, a novel system employing a solid-state fiber laser, EOSINT M 270, was first introduced to print stable and high-quality metal parts. Then, boosted by the increasing development of PBF, other companies started to develop their commercial LPBF equipment. For example, Concept Laser presented a machine named M3 Linear at the end of 2001 and coined the term “LaserCusing”; SLM Solutions introduced a more popular designation named SLM for their machines, which is commonly known among contemporary researchers and engineers; Trumpf introduced their commercial system named Trumaform LF 250 in 2003, which used a disc laser and included two separate build chambers with a preheating temperature of up to 500 °C.

3.2 Fundamentals

The LPBF process consists of several steps, from computer-aided design (CAD) model preparation to removing fabricated parts from the build platform. Before the CAD data are uploaded to the LPBF machine to produce parts, the stereolithography (STL) files must be processed to provide support structures for overhanging features and generate slice data for the laser scanning of individual layers. The printing process starts with spreading a thin layer of metal powder on a substrate plate by a recoater (roller or blade). After the powder is applied, one or multiple laser sources with high energy densities are employed to melt the selected areas. Once the laser scanning is completed, the build platform is lowered, and the next layer of powder is deposited on top. The laser then scans a new layer, and the process is repeated until the parts are completely printed.

The build chamber is protected with an inert gas flow (e.g. argon or nitrogen) during the printing process to prevent oxidation. In addition, the homogeneous gas that flows across the build area helps to remove the condensate (e.g. spatters and condensed metal vapor) produced during the powder melting process and plays a vital role in determining the quality and performance of the printed parts (Ferrar et al. 2012).

Once the process is completed, loose powder is removed from the chamber, and the parts can be separated from the substrate plate manually or by electrical discharge machining. The entire process is automated, except for the CAD data preparation process and the removal of the printed parts from the build platform. Schematic illustrations of the LPBF machine and produced melt pools are presented in Figure 3.1.

The distinct advantages of LPBF are presented as follows:

- The process involves a fine laser beam with a high beam quality, which carries sufficient energy to melt metals and ensures high printing accuracy. Its high manufacturing precision makes it suitable for directly printing complex structures with delicate features and smooth surfaces.
- The melt pools possess ultrahigh cooling rates, which vary with process parameters and materials in the range of 10^3 – 10^8 K/s, resulting in ultrafine microstructures and superior mechanical properties of the printed parts.

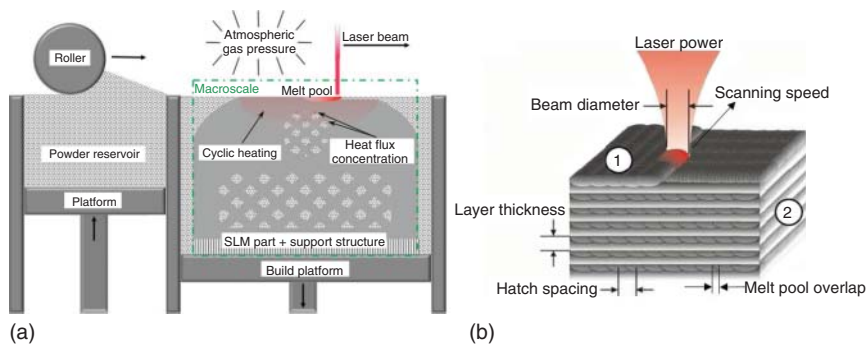


Figure 3.1 (a) Schematic illustration of an LPBF machine. Source: Reproduced from Meier et al. (2017)/with permission of Begell house Inc. (b) Schematic illustration of melt pools. Note that the scanning strategy depicted in this figure is bidirectional scanning with 90° rotation between each powder layer, and numbers 1 and 2 represent the horizontal and vertical build planes, respectively. Source: Reprinted with permission from a work by Vilaro et al. (2008).

- The process can manufacture parts with high relative densities (above 99%) from various metallic materials, such as titanium and its alloys, iron and steel alloys, nickel alloys, cobalt alloys, aluminum alloys, and copper and its alloys, to achieve high structural integrity.
- The cost and lead time of the production cycle can be reduced, especially for high value-added but low-production volume parts.

Meanwhile, the limitations of LPBF are:

- High residual stress is produced in parts resulting from the large temperature gradients. Therefore, post-heat treatment is often required to relieve the residual stress.
- Adding support structures to parts with overhanging features is necessary, and post-processing is required to remove these support structures manually.
- The size of printed parts is restricted due to the limited volume of the build chamber.
- The types of available powder materials are limited. Printing high-reflectivity powder materials, such as pure copper and pure aluminum, is challenging through infrared laser.
- The process is characterized by low production rates due to the powder recoating process.

Some limitations can be alleviated by developing industrial-oriented LPBF facilities with multiple laser beams and an extended build chamber. For example, SLM Solutions Group AG recently launched the industrial-scale NXG XII 600 equipped with envelope dimensions of 600 mm × 600 mm × 600 mm and 12 laser beams of 1000 W each, achieving a production rate 20 times faster than a standard single-laser LPBF machine. Moreover, ultrafine powder particles (e.g. <10 μm) employed in LPBF may introduce safety hazards such as particle inhalation and explosions.

In LPBF, process parameters can be classified into four categories: (i) laser-related parameters (laser power, beam spot size, pulse duration, pulse frequency, etc.), (ii) scanning-related parameters (scanning speed, hatch spacing, scanning strategy, etc.), (iii) powder bed-related parameters (powder bed density, layer thickness, etc.), and (iv) temperature-related parameters (powder bed temperature, substrate temperature, etc.). The optimized parameters vary with the machine and the powder material employed. Thus, parametric studies to optimize the parameters are essential for producing defect-free and fully dense parts. As illustrated in Figure 3.1b, the key process parameters include laser power, laser spot size, hatch spacing, scanning speed, scanning strategy, and layer thickness, and their selections are interdependent.

The laser absorptivity of different powder materials depends on the laser wavelength, which is further determined by the type of laser selected, as illustrated in Figure 3.2. Three types of lasers are commonly used in LPBF equipment: CO₂ laser, fiber laser, and diode-pumped neodymium-doped yttrium aluminum garnet (Nd:YAG) laser (Figure 3.2a). The CO₂ laser has relatively low power and absorptivity for metals and is generally selected for polymer-based LPBF. The fiber and Nd:YAG lasers perform similarly in metal printing and are widely utilized for commercialized metal-based LPBF equipment. Nevertheless, the applicability of the above two types of lasers is limited to certain metal materials. For example, iron and steel exhibit high laser absorptivity with respect to the fiber laser, which is a quality prevalent in modern LPBF equipment. In contrast, aluminum, copper, silver, and gold exhibit low laser absorptivity or high optical reflectivity at the laser wavelength of 1.07 μm . Fortunately, the laser absorptivity of certain reflective materials (such as copper) can be significantly enhanced using a green laser source, as shown in Figure 3.2b. Nevertheless, the green laser is still pending commercialization for LPBF equipment.

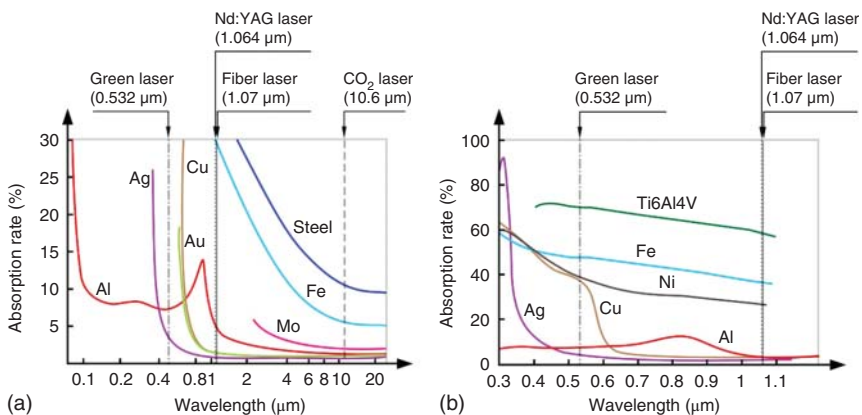


Figure 3.2 (a) Laser absorptivity of Al, Ag, Au, Cu, Mo, Fe, and steel with laser wavelengths from 0.1 to 20 μm . Source: Bergström (2018)/David Bergström. Note that the horizontal axis is logarithmic. (b) Laser absorptivity of Ag, Cu, Al, Ni, Fe, and Ti-6Al-4V with laser wavelengths from 0.3 to 1.1 μm . Source: Adapted from Alsaddah et al. (2021).

The hatch spacing refers to the overlap between adjacent melt tracks and determines the extent of metallurgical bonding between the tracks. Small hatch spacing often leads to excessive overlap and thus increases the fabrication time. On the other hand, large hatch spacing imposes limitations on the maximum layer thickness and increases the propensity of gap formation due to the lack of intra-layer bonding.

The layer thickness should be sufficiently large for a part to be manufactured cumulatively. However, the excessive thickness can introduce metallurgical defects, such as balling and lack of fusion, thus degrading the structural integrity and properties of the printed part.

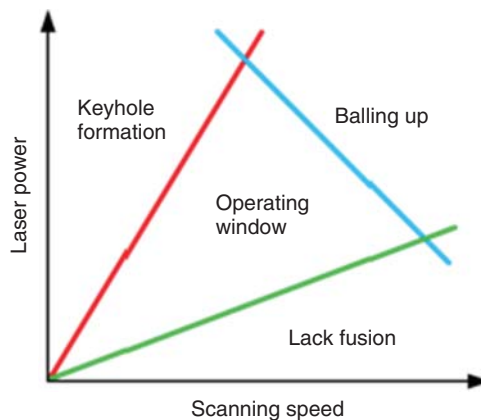
The laser power controls the amount of energy delivered to the irradiated material. Highly reflective materials (such as pure copper) require high power to be melted completely; otherwise, the resultant partial melting will cause the melt pool space to be filled incompletely upon solidification, thus introducing defects. In addition to regulating the melting efficiency, the laser power governs the size and continuity of a melt track, thereby affecting the structural integrity of the parts.

The scanning speed controls melting and solidification rates. The low speed extends the duration of irradiated spot maintained in a molten state, thereby slowing down the solidification process and affecting the microstructure and size of the melt track.

The powder material, laser spot size, and layer thickness are usually fixed for any given build, leaving the laser power, scanning speed, and hatch spacing to be optimized. However, the adjustable range of the hatch spacing is narrow in terms of practical applications, in which a balance must be achieved between the build rate and part quality. Hence, the combination of laser power and scanning speed is crucial for determining the process outcomes during LPBF printing, as illustrated in Figure 3.3.

The scanning strategy defines the spatial movement pattern of the laser beam. Various scanning strategies have been developed in pursuit of printing components with near-full density and controllable crystallographic texture. Four basic patterns, namely, unidirectional, bidirectional, stripe/paintbrush scanning, and island/chessboard/checkboard scanning, are commonly employed in LPBF for every single layer (Figure 3.4).

Figure 3.3 Effects of laser power and scanning speed on the process outcomes during LPBF printing.



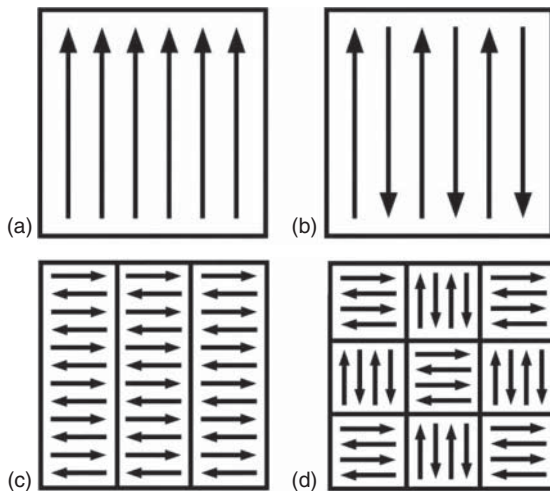


Figure 3.4 Four main basic scanning patterns in a single layer. (a) Unidirectional scanning, (b) bidirectional scanning, (c) stripe/paintbrush scanning, and (d) island scanning.

Unidirectional scanning is the most straightforward pattern in which the scanning process is performed in the same direction, which generally leads to the least densification but the strongest texture of a melt track. Bidirectional scanning is conducted by scanning in opposite directions for two adjacent lines, thus exhibiting a zigzag pattern. Stripe scanning is carried out by scanning bidirectionally within each parallel stripe. Island scanning adopts a checkerboard pattern of alternating bidirectional fills, which reduces temperature gradients in the scan plane by uniformly distributing the process heat.

Various scanning strategies can be employed for adjacent layers, including a rotation of the scan plane by a certain angle and a shift of the starting point by a certain distance between the layers (Figure 3.5). The choice of the scanning strategy also significantly affects the residual stress produced in printed parts. For example, the rotation of the scan plane on successive layers at an angle of 67° is commonly implemented, which can reduce warping, the number of defects, and the anisotropy of the printed parts. In addition, a remelting strategy (i.e. scanning a layer with the same path multiple times) can improve the surface quality of the printed parts.

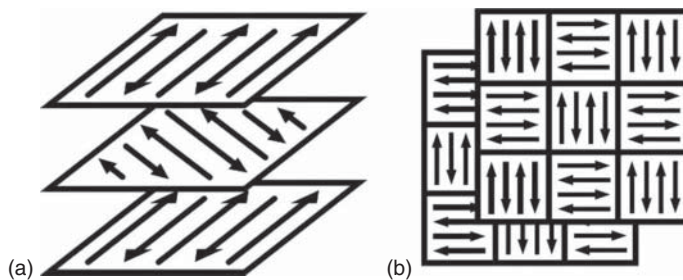


Figure 3.5 Scanning strategies in multiple layers. (a) Rotation of bidirectional scan vectors by a certain angle and (b) shifting a certain distance between the layers of an island scanning pattern.

The laser power, spot size, scanning speed, and powder bed temperature determine the energy input needed to melt the powder and form a desirable part. A lower laser power requires lower scanning speeds to ensure proper particle fusion. The hatch spacing should be carefully selected to provide sufficient melt pool overlap between adjacent tracks of fused material to ensure robust mechanical properties. The optimized hatch spacing is often set at $0.7 \omega_0$, where ω_0 is the diameter of the laser beam at its focus point (Cloots et al. 2016). The LPBF processing window changes for different metals because of variations in surface tension and viscosity of the melt and the melting point, chemical composition, laser absorption, and thermal conductivity of metals.

One of the metrics commonly employed for optimizing process parameters to obtain near-full dense parts is energy density, which is calculated based on a linear, areal, or volumetric approach. The volumetric approach is widely encountered in scientific literature.

The linear energy density E_l (J/mm) can be described by Gu et al. (2012b)

$$E_l = \frac{P}{v}, \quad (3.1)$$

in which P is the beam power (W), and v is the scanning speed (mm/s).

The surface energy density E_s (J/mm²) that is applied to the surface of the powder bed can be described by Das et al. (2010)

$$E_s = \frac{P}{vd}, \quad (3.2)$$

in which d is the laser beam diameter on the substrate (mm).

The volumetric energy density E_v (J/mm³) can be described by Kruth et al. (2005) and Thijs et al. (2010)

$$E_v = \frac{P}{vht}, \quad (3.3)$$

in which h is the hatch spacing (mm), and t is the layer thickness (mm).

A variation of the volumetric energy density E_v (J/mm³) can be described by Liu et al. (2015)

$$E_v = \frac{4P}{\pi vd^2}. \quad (3.4)$$

The optimization of process parameters is based on the energy density. However, these formulae do not consider other factors such as the thermal conductivity of the powder material, the time interval between printing consecutive layers, the scanning patterns and hatch spacing, the gas flow rate and direction within the process chamber, the scan offset at the corners and boundaries, and the number of times that a layer is scanned if remelting is applied.

3.3 Printing Process

LPBF involves heating and melting the metal powders with laser beams and rapidly solidifying the molten material to form the desired parts with complex thermal histories. Several critical phenomena are known to occur during the melting process,

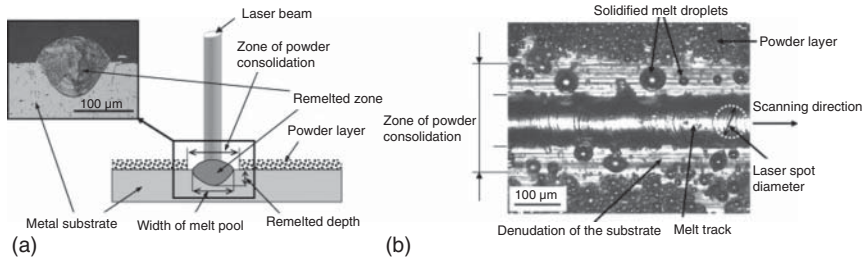


Figure 3.6 A melt pool produced by LPBF from the 316L stainless steel powder on a steel substrate. (a) Typical cross-sectional view and (b) top view. The laser power, scanning speed, and layer thickness were fixed at 50 W, 0.10 m/s, and 40 μm , respectively. Source: Yadroitsev et al. (2010)/reproduced with permission from Elsevier.

such as the absorption of the laser irradiation by the powder materials, heat transfer, melt flow, evaporation of materials, balling, spattering, phase transformation, and chemical reactions.

3.3.1 Melt Pool

Laser-matter interaction in LPBF is a controlled heating process in which the laser serves as a controllable heat source. When a laser beam impinges on a metal powder surface, the optical properties of the powder material determine the reflection, absorption, and transmission of light. The fraction of the laser beam absorbed by the surface of the metal powder is transformed into heat through electron-phonon interactions, and such heat raises the temperature of the surface to achieve the required molten state of the metal. Eventually, a tiny melt pool is produced on the surface of the powder bed (Figure 3.6) (Yadroitsev et al. 2010).

At the initial stage of LPBF, when the powder is still in its solid state, thermal conductivity is the main material property that influences the outcome. During laser processing, only a fraction of the radiation is absorbed by the particles at the surface of the loose powder layer. The rest of the radiation penetrates the voids between the powder particles of the layer and interacts with the underlying particles. Common heat transfer mechanisms (conduction, convection, and radiation) govern heat distribution within the powder layer. The intensity of the laser radiation decreases with its penetration depth into the powder layer. Metals with high thermal conductivity and reflectivity, such as aluminum and copper alloys, are generally harder to process than iron and steel alloys, titanium and its alloys, and nickel-based alloys. Therefore, higher laser intensities and shorter dwell times, which can be estimated by dividing the laser spot size by the laser scanning speed, are generally adopted to minimize conduction losses and obtain a sufficiently high temperature to create a melt pool.

There are three melting modes in LPBF that depend on the processing conditions, i.e. the conduction mode (Figure 3.7a), keyhole mode (Figure 3.7b), and transition mode (Figure 3.8). The threshold value for determining the mode depends on material properties and laser characteristics. As the power density increases above the

Figure 3.7 Representative melt pool morphology of LPBF-printed 316L stainless steel showing different melting modes. (a) Conduction mode and (b) keyhole mode. Source: Metelkova et al. (2018)/reproduced with permission from Elsevier.

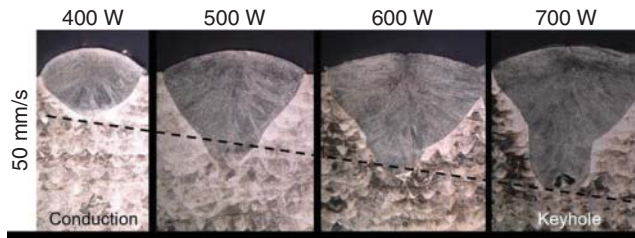
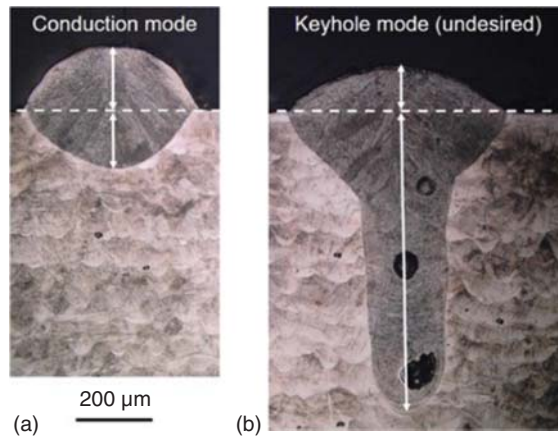


Figure 3.8 Representative melt pool morphology displaying the transition from the conduction mode to the keyhole mode of LPBF-printed 316L stainless steel with increasing laser power. Source: Metelkova et al. (2018)/reproduced with permission from Elsevier.

threshold value, the melting mode changes from the conduction mode to the transition mode to the keyhole mode.

Heat conduction is the dominant heat transfer mechanism for conduction mode melting. When the power density is lower than a particular threshold value, heat conduction is the dominant heat transfer mechanism, particularly for determining the depth of the melt pool created. The cross-section of melt pools created in the conduction mode is generally semicircular, but the depth of the melt pool is smaller than or equal to its half-width (Figure 3.7a).

Note that the vaporization of metals can be ignored in the conduction mode in conventional laser welding. However, it has been claimed to play a significant role in the conduction mode for LPBF (Patel and Vlasea 2020), which can be attributed to the reduced beam size in LPBF corresponding to a higher energy density and, therefore, the possibility of vaporization.

Heat convection is the dominant heat transfer mechanism for keyhole mode melting. When the energy density exceeds a threshold value, a deep vapor cavity forms within the molten metal due to intense localized heating and vaporization of the material on the surface of the molten metal. The depth of a melt pool is controlled

by the recoil momentum pressure (also known as recoil pressure) generated by the vaporization of the melt pool material. The top region of a keyhole mode melt pool resembles an hourglass and is wide due to the radially outward Marangoni flow. In contrast, its bottom region is narrow and resembles the shape of a keyhole. The melt pool depth in keyhole mode laser melting is typically greater than the half-width of the melt pool defined at the top of a given melt pool (Figure 3.7b).

The transition mode of melting in LPBF lies between the conduction and keyhole modes (Figure 3.8), in which the dominance of conduction or convection depends on the processing conditions.

The threshold for these three modes depends on the laser absorptivity and thermal conductivity of the material. For materials with average absorptivity and conductivity, the threshold is 0.5 times the beam spot radius for the vaporization depth from conduction mode to transition mode and 0.8 times the beam spot radius for the vaporization depth from transition mode to keyhole mode. However, for high-reflectivity and high-thermal conductivity materials such as aluminum alloys, the threshold value is lowered to 0.5 times the beam spot radius for the vaporization depth from the transition mode to the keyhole mode. In contrast, the transition mode melting can occur with surface vaporization alone.

The melt pool is characterized by melt pool temperature, temperature gradient, lifetime of melt, melt pool dimensions, melt viscosity, melt flow, melt pool stability, and balling and spattering due to melt pool instability. The formation of a melt pool and its characteristics are fundamentally determined by the energy absorbed by the powder bed as the laser beam passes. The microstructure of a solidified melt pool is divided into three regions: (i) the melt pool core, where the cells are finer and exhibit a more equiaxed structure, (ii) the melt pool boundary, where the cells are coarser and mostly elongated, and (iii) the heat-affected zone.

The melt pool temperature and temperature gradient are primarily determined by the energy density. For example, the maximum temperature increases with the linear energy density but slightly decreases with the laser scanning speed (Dai and Gu 2014). The most comprehensive understanding of the temperature profiles has been achieved through computational modeling. As shown in Figure 3.9, the highest temperature gradients appeared within the melt pool soon after the laser scanning commenced (Khairallah et al. 2016). For a laser power of 200 W and a scanning speed of 1.5 m/s, the surface melt pool shape settled into a quasi-steady state of 225 μ s after scanning. Another investigation illustrated that temperatures, thermal gradients, and cooling rates in the range of 1000–4000 K, 5–20 K/ μ m, and 1×10^6 – 4×10^7 K/s, respectively, were measured for the melt pools of Ti–6Al–4V through a high-speed imaging thermography method with a resolution of 20 μ m (Hooper 2018). They were observed to vary with the process parameters, part geometry, and location in the scan path. The temperature gradient in the melt pool is steeper in materials with low thermal conductivity and increases linearly with the applied laser power. The lifetime of the melt pool refers to the duration between the powder particles in the local region melting and solidifying. The melt pool lifetime can be extended by increasing the laser power or decreasing the scanning speed.

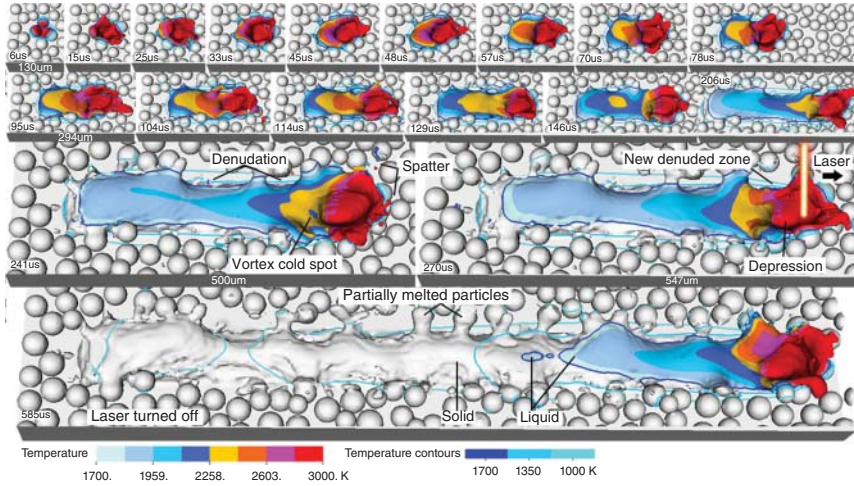


Figure 3.9 Time snapshots presenting the surface temperature evolution in a melt pool of 316L stainless steel. The scanning speed and power of the laser were 1.5 m/s and 200 W, respectively. Source: Khairallah et al. (2016)/reproduced with permission from Elsevier.

The dimensions of the melt pool include its length, width, and depth, which are functions of the absorbed energy density. The influence of linear energy density E_l on the melt pool length and width is more significant than that on the melt pool depth.

Melt flow can be applied to describe the dynamics of melt pools. Mass transfer in melt pools occurs because of the thermocapillary flow, and large temperature gradients produce surface tension gradients within melt pools. The sign of the surface tension gradient $d\gamma/dT$ determines the direction of the melt flow, where γ is the surface tension and T is the temperature. As shown in Figure 3.10, if $d\gamma/dT < 0$, the flow extends radially outward, and a desirable shallow and broad melt pool is produced; if $d\gamma/dT > 0$, the flow is directed radially inward, and a narrow/deep melt pool is formed.

Melt pool stability is responsible for the quality of LPBF-fabricated parts. The range of stable zones in melt pools increases with the laser power, and it becomes narrower for materials with higher thermal conductivity (Yadroitsev et al. 2010). The instability of melt pools results in an irregular and/or discontinuous track, which is derived from hydrodynamic instability and capillary (Rayleigh) instability. The hydrodynamic instability of a melt pool is driven by the Marangoni effect. The Marangoni instability of the flow within a melt pool can be estimated from the dimensionless Marangoni number M_a :

$$M_a = \frac{d\gamma}{dT} \frac{dT}{dr} \frac{L}{2\eta\delta}, \quad (3.5)$$

where dT/dr is the temperature gradient, L is the characteristic length of the melt pool, η is the viscosity, and δ is the thermal diffusivity (Lu et al. 2004). The capillary instability implies the break-up of a liquid cylinder with a high aspect ratio to reduce the surface energy. It occurs when the total surface area of the melt pool is larger than that of a sphere of the same volume and when the viscosity of the liquid is too low.

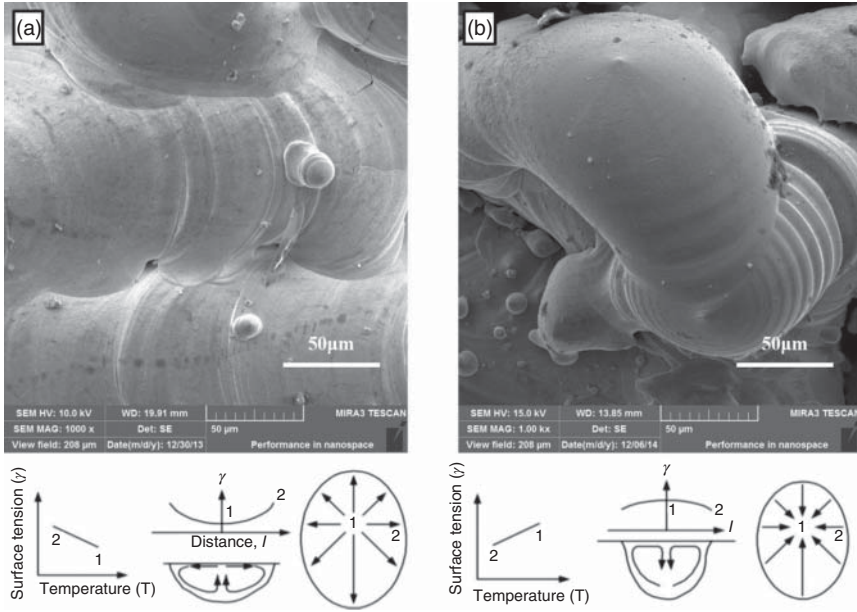


Figure 3.10 Effect of melt flow on the melt track formation of tungsten printed by LPBF. (a) $d\gamma/dT < 0$ and (b) $d\gamma/dT > 0$. Source: Zhou et al. (2015a)/reproduced with permission from Elsevier.

Therefore, it is vital to control the ratio of the length l and the width d of the melt to meet $l/d < 2.1$ (Kruth et al. 2004). The break-up time t is equal to

$$t = \{0.3433\sqrt{\gamma/[\rho(W/2)^3]}\}^{-1}, \quad (3.6)$$

where ρ is the liquid density, and W is the diameter of the melt pool. The expression reveals that alloying elements with only a change in γ do not significantly alter the dynamics of the capillary instability because such a change only affects t on the order of one-tenth of a millisecond. However, a higher viscosity increases the break-up time and results in larger droplets with larger spacings between the droplets. The melt pool instability easily results in a balling phenomenon.

3.3.2 Balling

Balling is characterized by the melt track shrinking and breaking up into a row of liquid spheres to reduce the surface energy due to surface tension when the molten material does not wet the underlying substrate.

Ellipsoidal and spherical balls can be observed in the balling phenomenon of LPBF. The ellipsoidal balls are large with equivalent diameters of $\sim 500 \mu\text{m}$, which are detrimental to the quality of LPBF parts. In contrast, the spherical balls are much smaller, with diameters of $\sim 10 \mu\text{m}$, and they have little impact on the printed parts (Li et al. 2012). The large-sized ellipsoidal balls can be produced due to a limited amount of molten metal formed and a low undercooling degree of melt

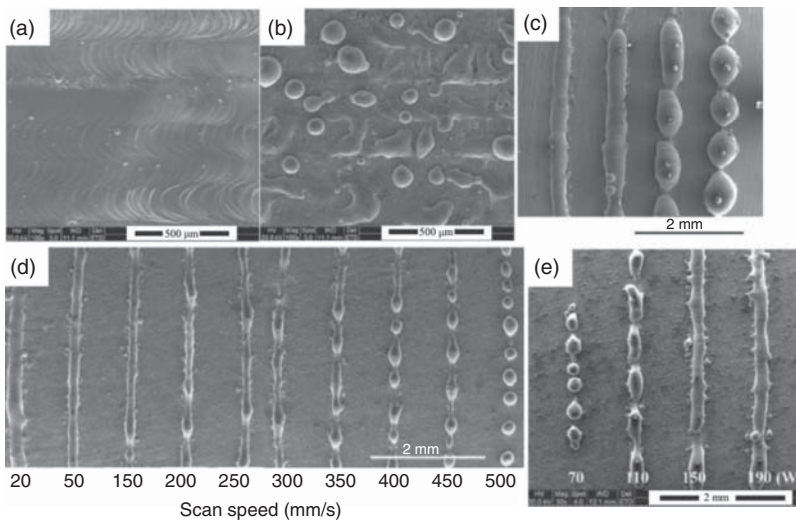


Figure 3.11 Balling phenomenon in LPBF resulting from different mechanisms due to changes in various process parameters. (a) 0.1% and (b) 10% oxygen content, (c) layer thickness (increasing from left to right), (d) scanning speed, and (e) laser power. Source: Li et al. (2012)/reproduced with permission from Springer Nature.

at a low laser power; the small-sized spherical balls are formed by laser-induced splashes due to excessively high energy input (Gu and Shen 2009).

The balling phenomenon severely degrades the material properties and printed part geometry. It severely impedes the uniform spreading of fresh powder onto the previously solidified layer and can potentially induce porosity and even delamination resulting from poor interlayer bonding combined with residual stress. It might even jeopardize the powder-spreading process if the size of the balls is sufficiently large to interfere with the movement of the recoater.

The formation and morphology of balling are influenced by parameters including oxygen content, layer thickness, scanning speed, and laser power during SLM printing, as summarized by Li et al. (2012) (Figure 3.11).

The balling phenomenon can be alleviated by decreasing the oxygen content in the atmosphere (Figure 3.11a,b), as oxidation of the melt pool can reduce the wettability of the liquid at the wetting surface. A large layer thickness is unfavorable for wetting melt pools (Figure 3.11c), as the laser energy absorbed in a unit volume of powder and the contact between powder particles and the substrate are both insufficient. Under a given laser power, increasing the scanning speed results in forming a narrower melt track, which eventually breaks into discontinuous balls (Figure 3.11d). For a given scanning speed, a lower laser power results in a smaller amount of liquid forming, while a higher laser power facilitates the wetting and spreading of melt pools (Figure 3.11e).

In contrast, excessive energy density resulting from a combination of high laser power and low scanning speed may cause self-balling. This combination results in excessive liquid formation and a long melt pool lifetime. Consequently, a

considerably lower melt viscosity, a higher degree of superheat of the low melting phase, and an enhanced Marangoni effect are achieved, thereby producing a large number of individual small balls.

The balling phenomenon often occurs during the solidification of the first melt pool of the first layer on a cold substrate, which is also known as “first-line scan balling”. The high and steep thermal gradient between the molten material and unmelted powder particles results in a significant increase in the surface tension of the melt pool. Consequently, the melt pool tends to break into spherical metallic agglomerates to minimize surface energy. First-line scan balling can be alleviated by increasing the powder bed temperature. The presence of a low-temperature gradient in this instance leads to lower surface tension of the melt, which restricts the capillary instability and reduces the tendency of first-line scan balling.

In addition to optimizing the process parameters, the balling phenomenon can also be alleviated to a certain extent by remelting the surface, through which the metal balls can be melted to wet the surface more favorably. Nevertheless, this strategy is not widely adopted in industrial applications as it significantly lowers productivity due to the prolonged scanning time.

3.3.3 Spattering

Spattering is a common phenomenon caused by the interaction between the laser and powder bed during the LPBF process, which can lead to the high-speed escaping of powder particles and metal droplets from melt pools. The heat in melt pools is difficult to transmit to the surrounding materials, which results in the temperature of the exposed powder particles exceeding the melting temperature. A further increase in temperature induces the vaporization of the material. During this stage, the rapidly moving vaporized materials expand and generate recoil pressure on the melt pools. While a low recoil pressure facilitates the flattening of the melt pools, a high recoil pressure leads to the removal of molten material by melt expulsion and creates a metallic jet. The ejected metallic jets are disintegrated by the metallic vapor and broken down into micro-droplets when passing through the laser irradiation field to form spatters.

At the starting point of the scanning path, the laser began to strike the powder bed. However, the melt pool was not produced yet, and the vaporization and glare (i.e. the light intensity) were insignificant, as shown in Figure 3.12 (Liu et al. 2015). When the laser beam moved to the middle of the scanning path, the melt pool reached a dynamic equilibrium state, and the glare became steady. When the laser beam moved to the end of the scanning path, it slowed down, and the powder particles absorbed more energy, which dramatically enhanced the vaporization and glare.

The intensity of spattering increases with an increase in the energy density. At a low energy density, the spattering behavior is extremely insignificant as the temperature in the melt pools does not exceed the vaporization point, and almost no metallic vapor is generated. With an increase in the energy density, the extent of the metallic jet, droplets, and sideways spattering increases (the unmelted powder particles around the melt pools are dispersed due to the impact of the metallic vapor, which is

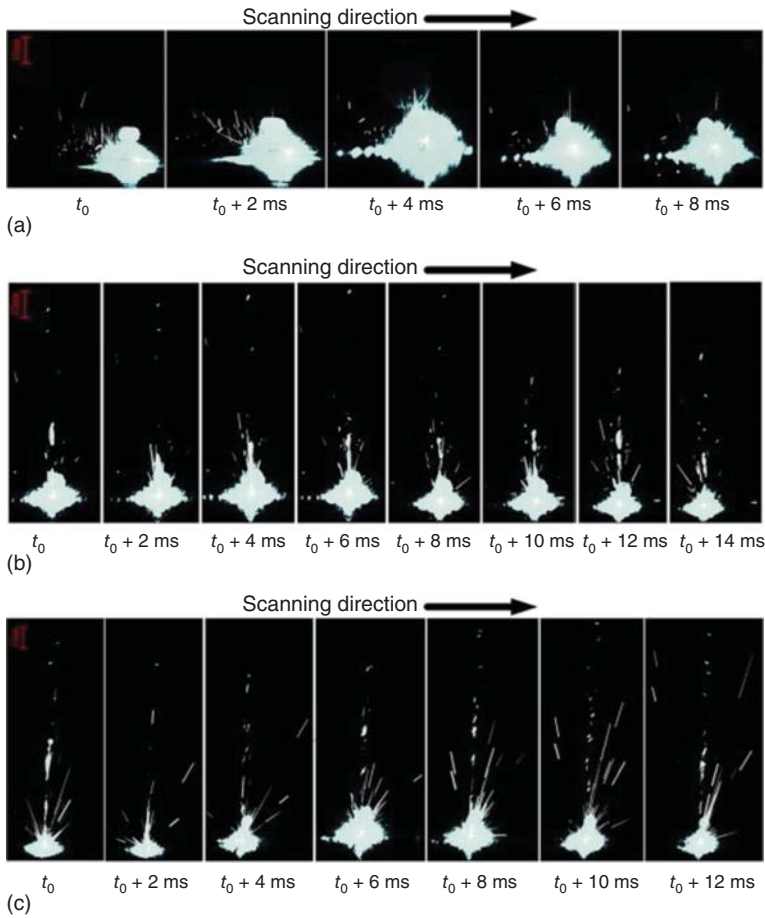


Figure 3.12 Spattering behaviors during the LPBF printing of 316L under different energy inputs. (a) 0.26×10^6 W/cm³, (b) 0.52×10^6 W/cm³, and (c) 0.78×10^6 W/cm³. Source: Liu et al. (2015)/reproduced with permission from Elsevier.

known as sideways spattering). At an extremely high energy density, the intensity of spattering oscillates periodically, which can be attributed to the produced metallic vapor absorbing a portion of the incident laser energy and forming a cloud consisting of small metal particles. This cloud arises from the condensation of hot metallic vapor, preventing most of the laser radiation from reaching the metal powder bed effectively.

Liquid droplets and unmelted powder particles around melt pools are expelled by the recoil pressure generated on melt pools resulting from the melt vaporization. The spatters resulting from melt expulsion are spherical, and they mix with the metal powder and spread onto the previously solidified layer, resulting in the balling phenomenon. The spattering caused by the expulsion of unmelted particles is also known as satellites. When such satellites fall on the powder bed, their excessively large sizes prevent them from fully melting by the laser beam, thereby becoming

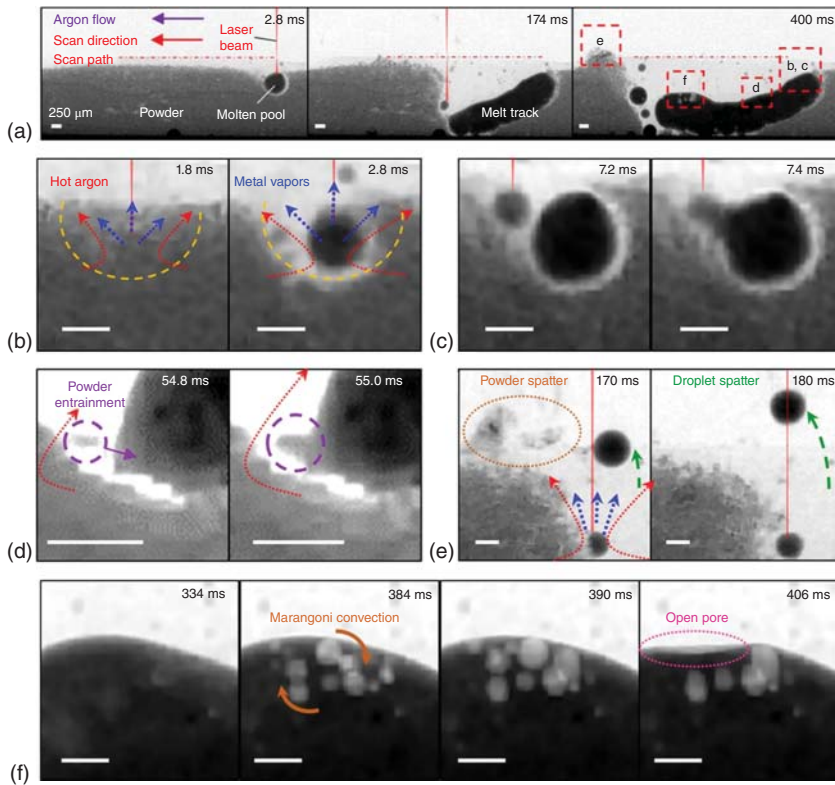


Figure 3.13 Time-series radiographs acquired during the LPBF printing of an Invar 36 single-layer melt track. (a) Melt track morphology at three key stages of LPBF, (b) formation of a melt pool and a denuded zone, (c) melt pool wetting, (d) vapor-driven powder entrainment, (e) powder spatter and droplet spatter, and (f) pore nucleation, coalescence, and collapse. All scale bars are 250 μm. Source: Leung et al. (2018)/reproduced with permission from Springer Nature, CC BY 4.0.

inclusions that form irregular pores in the subsequent layer. Additionally, oxides of a few micrometers in size on the spatter surface resulted from oxidation of the most volatile alloying elements enriched on it (Simonelli et al. 2015).

A comprehensive evolution of a single melt track can be elucidated by an *in situ* and operando synchrotron X-ray imaging method, as shown in Figure 3.13 (Leung et al. 2018). Invar 36 powder appears light gray, while the melt pool and melt track are dark gray because their effective density is almost twice that of the powder. Hence, they attenuate more X-rays. In Figure 3.13a, the laser consolidated powder particles into a liquid melt pool ($t = 2.8$ ms). The melt pool subsequently evolved into a melt track that extended toward the bottom of the powder bed. As the melt track cooled, it bent upward and formed pores in the last solidified region of the melt track ($t = 400$ ms).

Multiple steps are involved when a melt pool transforms into a melt track. During the initial stages of LPBF, a melt pool with a diameter of 100 μm formed below

the powder bed surface and rapidly grew into a sphere with a diameter of 250 μm . Powder spattering removed a significant amount of powder particles ahead of the laser beam, forming a denuded zone in front of the melt pool, corresponding to fewer powder particles available for the subsequent powder consolidation. As a result, the laser beam moved ahead and formed a new melt pool further along the scan path. The growth rate of this newly formed melt pool was higher than the scanning speed, thus resulting in the laser beam heating the melt pool while lowering its surface tension. Consequently, the newly formed melt pool coalesced with the first melt bead via wetting, revealing a key track growth mechanism.

Serious spattering often induces metallurgical defects (e.g. porosity and cracks) in printed parts. Effective methods, such as optimizing laser process parameters and adding nanoparticles to powder, have been demonstrated to alleviate the spattering during the LPBF process.

3.4 Metallurgical Defects

Metallurgical defects in LPBF, such as pores, cracks, and warping, are commonly observed in the final printed metal parts. These defects reduce the part density and act as stress risers, which adversely affect the properties and performance of the parts. The classification, formation mechanisms, and suppression strategies of these defects are comprehensively introduced in this section.

3.4.1 Porosity

Parts printed by LPBF typically contain more pores than those manufactured by conventional methods (Sames et al. 2016), which severely limits their applications. The buoyant force cannot effectively eliminate pores in melt pools (Weingarten et al. 2015), despite being a commonly employed mechanism that eliminates pores from a liquid. The high drag force induced by the strong melt flow in the LPBF process traps pores within the melt pools. Based on pore formation mechanisms, porosity in LPBF-printed parts can be classified into gas pores, keyhole pores, lack-of-fusion pores, lack-of-material-induced pores, and balling-induced pores.

Gas pores are produced by entrapped gases and are spherical. Firstly, if a metal powder has a low packing density, the gases between the powder particles may dissolve into the melt pools. The dissolved gases cannot escape from the surface of the melt pools because of the high cooling rate during solidification, and thus they form spherical pores. Secondly, gas bubbles can be induced at a high laser energy input due to the vaporization of volatile elements, which can be far beneath the surface at the bottom of the melt pools. These gas bubbles cannot escape from the surface, and thus they form regular spherical pores during the rapid solidification of the LPBF process. Thirdly, gas pores can be inherited from gas-atomized powder (Figure 3.14a). During powder preparation, inert gases, such as argon and helium, are inevitably introduced into the powder materials. As a result, gas pores are

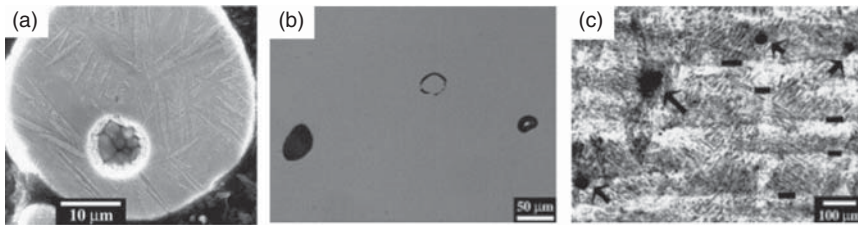


Figure 3.14 Typical morphology of gas pores in: (a) a Ti-6Al-4V powder particle, and (b, c) LPBF-printed Ti-6Al-4V samples. Source: Qiu et al. (2013)/reproduced with permission from Elsevier.

randomly distributed in an LPBF part, and their typical morphology is shown in Figure 3.14b,c.

Keyhole pores are generally produced at the start/end points of a steep and deep melt pool after its solidification when the laser energy density is excessive (Cunningham et al. 2019). As shown in Figure 3.15, pores form at laser turning points because of the emergence and collapse of a deep keyhole depression, which are caused by the deceleration and acceleration of the galvanometer-based scanning mirrors (a common mechanical component for controlling the scanning of the laser beam) during the turn. As the laser accelerates away from the turning point, the keyhole depression

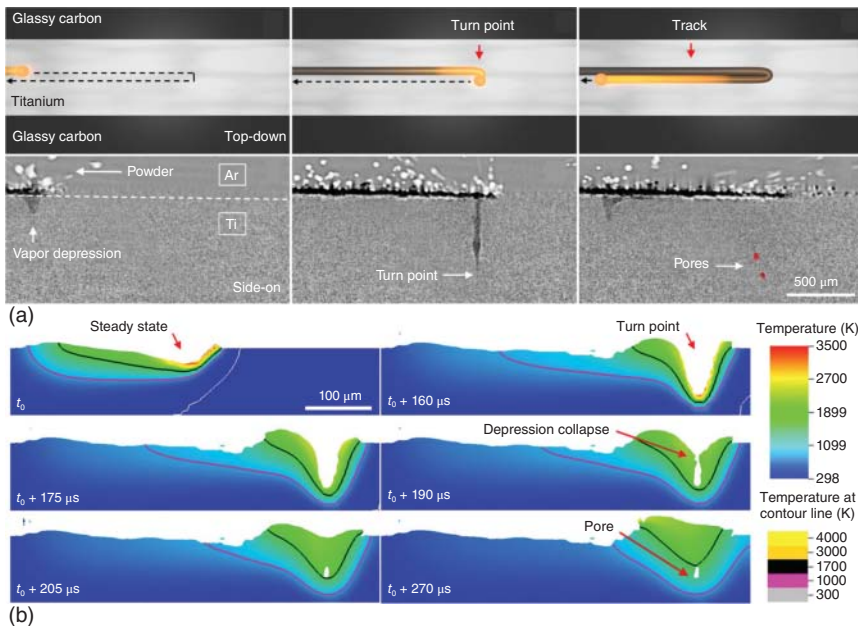


Figure 3.15 Formation of keyhole pores harnessed by *in situ* X-ray imaging and multi-physics modeling. (a) Description of a laser turning point in Ti-6Al-4V performed at a laser power of 200 W and a scanning speed of 1000 mm/s; (b) cross-sections of turning point dynamics from multi-physics simulation. Source: Martin et al. (2019)/reproduced with permission from Springer Nature, CC BY 4.0.

collapses and molten metal fills the void, thereby trapping the argon gas and ultimately forming a pore as the material solidifies (Martin et al. 2019).

More specifically, as the laser beam approaches the end of the track and decelerates, the vapor depression depth increases, which is a direct result of the increase in laser dwell time as the scanning speed decreases for the execution of the turn. More energy is absorbed by the track locally, causing the depth to increase. A more pronounced increase in depth occurs as the turn is completed, which is attributed to the accumulated residual heat being higher than at the entrance of the turning point. Immediately after reaching the maximum depth of the melt pool, the vapor depression depth rapidly decreases as the laser beam accelerates away from the turning point. The significant increase in vapor depression depth due to overheating followed by the rapid collapse gives rise to keyhole formation, as the liquid metal cannot fill the deep vapor depression before rapidly solidifying due to the extreme cooling rate ($\sim 10^6$ K/s). This behavior is universal and occurs regardless of the material at turning points during LPBF.

The mitigation of keyhole pore formation must satisfy the following mechanical and physical requirements: (i) the vapor depression must not transit into the keyhole regime at the turning points, (ii) the laser power must be controlled with no rapid oscillations to maintain a relatively stable energy output, and (iii) the laser power must not rapidly increase when accelerating out of the turning point into the preheated region.

Lack-of-fusion pores with irregular shapes are produced because of the lack of energy input, as shown in Figure 3.16. The metal powder is not fully melted and is thus unable to sufficiently bond to the adjacent solidified layer. The low laser energy input may also lead to the small width of melt pools, which results in an insufficient overlap between the melt tracks. The inadequate overlap induces the presence of unmelted powder particles between the tracks. In the spreading process of a new layer, it becomes difficult to fully remelt these powder particles. Therefore, lack-of-fusion holes are generally formed between the layers of LPBF-printed parts.

The lack of powder materials within a printing layer, which may be derived from uneven powder spreading on solidified printing layers or the powder bed, can induce irregular pores. For example, in a local area where defects such as warping and swelling deformation were generated, the surface of a solidified layer became rough (Zhou et al. 2015b). The rough surface directly contributed to poor powder spreading for the subsequent few layers and poor flow of the molten metal, hence forming interlayer irregular pores that led to significant multilayer defects in the continuous printing process.

Moreover, the oxidation of materials with a high affinity toward oxygen, such as Al-Si10-Mg, can lead to the localized delamination of layers and the formation of irregular pores. An oxide layer is usually formed on the surface of a part due to residual oxygen in the LPBF process. As the wettability of the surface decreases, the molten metal flow is blocked, leading to poor bonding between the layers and introducing fusion defects (Zhang et al. 2017).

Balling-induced pores are derived from the shrinkage of melt pools and spattering, which are caused by incomplete melt flow and excess energy inputs, respectively.

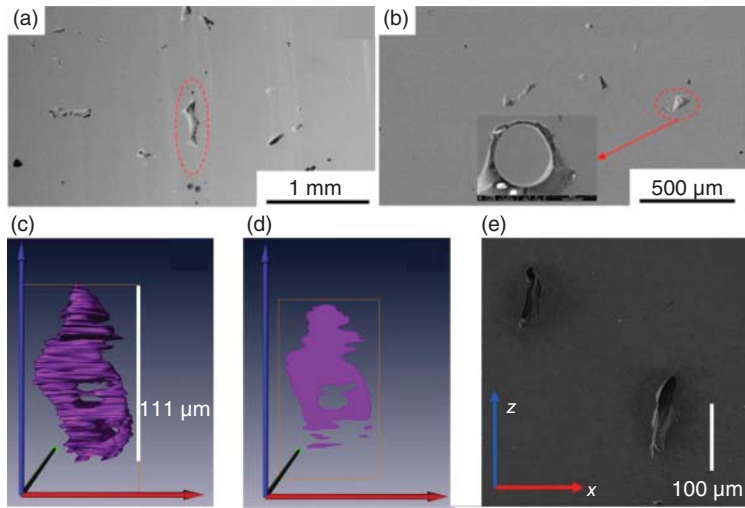


Figure 3.16 Secondary electron images for lack-of-fusion pores in LPBF-printed Al–Si–Mg alloys with volumetric energy densities of (a) 28.66 J/mm^3 and (b) 31.75 J/mm^3 . Source: Yang et al. (2018a)/reproduced with permission from Elsevier. Morphology of lack-of-fusion pores in LPBF-printed Co–Cr–Mo alloys. (c) 3D reconstructed top view in the x – z plane, (d) cross-section image, and (e) SEM image of the top view. Source: Zhou et al. (2015b)/reproduced with permission from Elsevier.

Particles from excessively large spattering may not be completely melted, thereby creating irregular pores in the following layers. In most studies, pores can be suppressed by optimizing the process parameters of LPBF. The porosity increased with an increase in the scanning speed. The pores produced from the combination of higher laser power and larger scanning speed were smaller and more circular in shape, which was attributed to the balling effect and high thermal stress cracking; pores produced under lower energy density were filled with unmelted powder particles due to insufficient melting.

The pore motion during printing needs to be understood. One representative research unveiled that the micropore motion is governed by the competition between the temperature gradient-induced thermocapillary force and the melt flow-induced drag force (Hojjatzadeh et al. 2019). As presented in Figure 3.17a, in the region near the laser beam, the micropores moved toward the depression zone and escaped from the melt pool. This region is called the laser interaction domain. Further away from the laser interaction domain, the micro-pores were circulated within the melt pool. This region is called the circulation domain. Between these two regions, a region called the transition domain existed. In this region, the micropores moved randomly, i.e. occasionally moving toward the surface of the melt pool and escaping, while at other times circulating.

In the laser interaction domain, the temperature gradient exhibited an average value of $6.5 \times 10^7 \text{ K/m}$ with a direction approximately normal to the melt pool boundary. Such a high temperature gradient resulted in a thermocapillary force at least three times higher than the melt flow-induced drag force. The thermocapillary

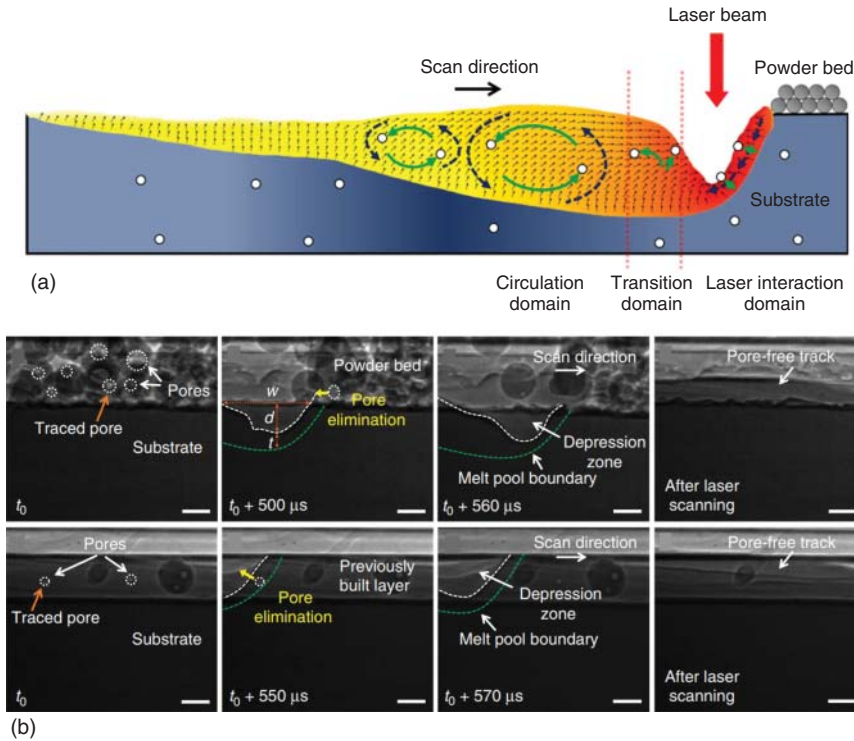


Figure 3.17 (a) Schematic illustration of the dynamics of pore motion and mechanisms of pore elimination during LPBF, and (b) dynamic X-ray images showing the elimination of pores through the application of thermocapillary forces. All scale bars are 50 μm . Source: Hojjatzadeh et al. (2019)/reproduced with permission from Springer Nature, CC BY 4.0.

force drove the melt around the micropore to flow from the hot region to the cold region, resulting in the micropore movement in the opposite direction. Thus, the thermocapillary force is the dominant force in the laser interaction domain, which drives the micropores to move in the direction of the temperature gradient, while the drag force arising from the melt flow controls micropore motion in the circulation domain.

The pore elimination mechanism driven by the thermocapillary force can serve as an effective approach to eliminate micropores during the LPBF process. It has been validated to eliminate micropores in the feedstock powder and the previously printed layer to achieve a pore-free track, as shown in Figure 3.17b. The proper laser process parameters are determined based on the following two general guidelines. First, the temperature gradient in the laser interaction domain is sufficiently high to overcome the melt flow-induced drag force. The temperature gradient around the laser interaction domain can be estimated by the difference between the boiling temperature T_b and melting temperature T_m of the material over the thickness t of the liquid layer around the depression zone, i.e. $(T_b - T_m)/t$. For a given material, a smaller t indicates a higher temperature gradient. Second, the area of the high-temperature

gradient region should be reasonably large to provide a high possibility of encountering pores. This area is a large laser interaction domain, defined by the width w over depth d ratio of the depression zone, w/d . An excessively small depth d indicates a shallow melt pool and may cause lack-of-fusion pores.

Careful optimization and control of the printing parameters are indispensable to minimizing the porosity of LPBF-printed parts. In general, a relative density of 99% and above can be reached by LPBF for various materials. It was reported that the formation of linear-shaped pores in Ti-6Al-4V was attributed to insufficient melting, resulting from improper optimization of process parameters or an irregular powder bed thickness (Vilaro et al. 2011). These pores are typically larger (100–150 μm in length) than spherical pores. Irregular or clustered pores may lead to stress concentration. Therefore, the pores are expected to significantly degrade mechanical properties compared to spherical pores (Maskery et al. 2016). Similar results have been obtained through synchrotron radiation micro-tomography for LPBF-printed 316L stainless steel (Carlton et al. 2016).

On the other hand, a remelting approach, in which a layer is melted a second time before depositing the next powder layer, was validated to reduce residual porosity in LPBF-printed 316L from 0.77% to 0.036% (Yasa and Kruth 2011). In the study, the irregular-shaped pores between the melt pools were shown to close once the material was remelted. Moreover, remelting led to further grain refinement due to the relatively high heat conduction in the consolidated material compared to the initial powder. Nevertheless, remelting lowers productivity in industrial applications.

In addition to process parameter optimization, post-processing can also be done to minimize porosity. A representative study indicated that most of the residual pores in LPBF-printed Ti-6Al-4V can be effectively eliminated by applying hot isotropic pressing (HIP) (Qiu et al. 2013). Nevertheless, HIP cannot suppress open pores and excessively large closed pores. Furthermore, the geometrical accuracy of the LPBF-printed parts may also be negatively affected by the usage of HIP (see Chapter 1 for further details on HIP).

3.4.2 Cracks and Warpage

Macro- and micro-cracks often exist in LPBF-printed parts. Macro-cracks may be related to cold cracks resulting from the brittleness of the material and the delamination of adjacent printing layers within parts due to residual stresses when the parts rapidly cool down to room temperature. On the other hand, micro-cracks may be induced during solidification due to thermal stresses and the formation or dissolution of precipitates along the grain boundaries. The crack density depends mainly on the laser power because the temperature profile depends more on the laser power than the scanning speed; hence, steeper temperature gradients produced by high laser energy densities increase the magnitude of thermal stress, thereby promoting solidification cracking.

Residual stresses are internal stresses within a solid material. Such stresses are present even after all external loading forces have been eliminated, resulting from the equilibrium obtained after the plastic deformation of the material (Withers and

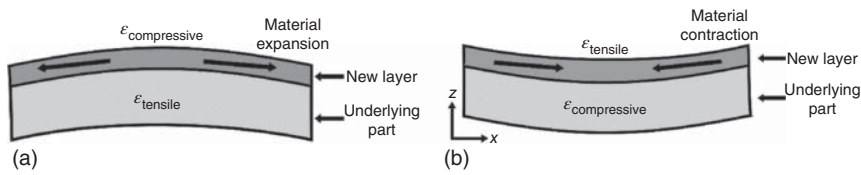


Figure 3.18 Basic mechanisms of stress and plastic deformation development during LPBF. (a) During heating and thermal expansion of the new layer and (b) during cooling and thermal contraction of the new layer. Source: Adapted from Mercelis and Kruth (2006).

Bhadeshia 2001). Residual stresses are usually classified by the length scale on which they operate. Type I residual stresses are macroscopic stresses that act on the geometry of parts and may cause global distortion. Type I stresses directly impact the fatigue properties of the produced materials, resulting in distortion during or after production. Therefore, they are extensively researched. Type II residual stresses are microstresses acting on an individual grain, often known as intergranular stresses. These stresses form because of local microstructural effects, such as grain-to-grain differences in slip behavior. Type III residual stresses are at the atomic scale and are considered misfit stresses due to vacancies, substitutional atoms, etc.

Large and anisotropic Type I stresses commonly exist in LPBF parts because of the large thermal gradients present during processing. Figure 3.18 presents a simplified case of a part produced through LPBF, during which entire layers are melted instantaneously (Mercelis and Kruth 2006). The layers printed up to this point, referred to as the “underlying part” in Figure 3.18, are cooled uniformly with a temperature gradient in the build direction. When a new layer is added and heated above the temperature of the underlying part, the new layer first expands uniformly. However, this expansion is restricted by the much cooler underlying region, resulting in compressive stresses in the new layer and tensile stresses in the underlying region (Figure 3.18a). When the heat source is removed, the new layer cools down rapidly, and the underlying region cannot accommodate such a high rate of contraction, resulting in tensile stresses in the new layer and compressive stresses in the previous layer (Figure 3.18b).

More specifically, during the solidification of the liquid melt, the cooler underlying material restricts the contraction of the melt and pulls on the solidifying region (opposite to the contraction direction); meanwhile, the rapidly solidifying melt tends to pull the underlying material inward during solidification. Since the material has sufficiently melted into the underlying part and assuming that strong metallurgical bonding occurs, strain must be accommodated between these regions and form residual stresses. As described, the stresses in the new layer are primarily tensile, and the resulting residual stress imposed on the underlying material is predominantly compressive. During solidification, the plastic strain that developed can be thought of as hydrostatic contraction, directed inward from every point of the liquid melt. It is noted that nonuniform melt pool geometries and solidification rates can be attributed to the inherent temperature gradient and melt pool motion altering the magnitude of stresses developed in each direction.

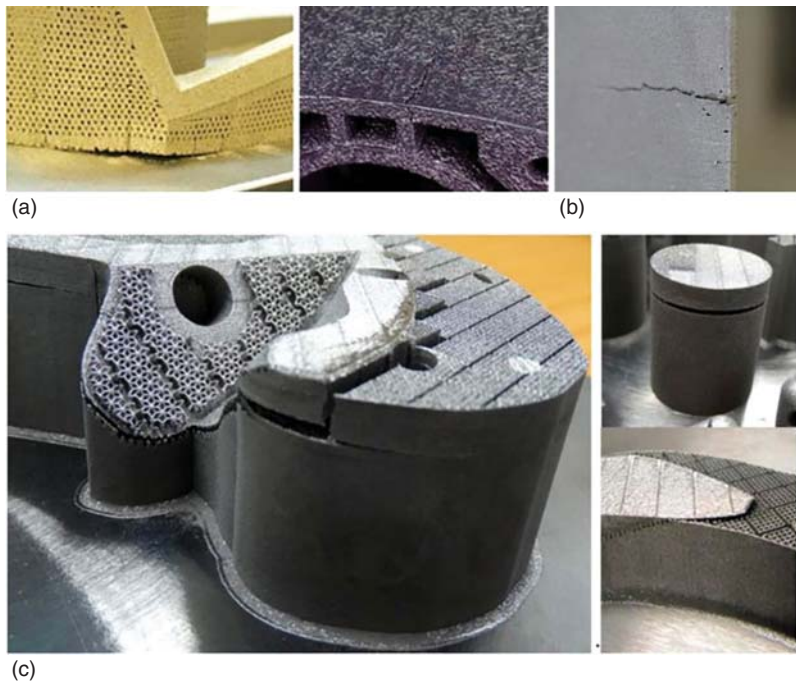


Figure 3.19 Cracks induced by residual stresses in LPBF-printed metal parts. (a) Tool steel 1.2709. Source: Zaeh and Branner (2010)/reproduced with permission from Springer Nature. (b) Ti-6Al-4V. Source: Parry et al. (2016)/reproduced with permission from Elsevier. (c) Ti-6Al-4V. Source: Yadroitsev and Yadroitsava (2015)/reproduced with permission from Taylor & Francis.

LPBF-printed parts are constantly under tension, with maximum stress located at the surface of the parts. The final residual stress on the parts increases with the number of layers built. The residual stress distribution along the build direction for a part removed from its substrate consists of a zone of tensile stresses just below the upper surface, followed by a large zone subjected to compressive stress, and subsequently a tensile stress zone at the bottom. The magnitude of the stresses depends on the part height and the stiffness and height of a substrate. The typical cracks resulting from residual stresses are shown in Figure 3.19.

The process parameters of LPBF have a critical influence on the magnitude and distributions of residual stress in the parts. Among these parameters, the scanning strategy effect has been investigated extensively as the scan vector length plays a significant role in determining the residual stress. For example, an island scanning strategy with a short scanning length can be advantageous for obtaining low residual stress (Li et al. 2018c). In addition, a suitable rotation angle of the laser scanning direction for the adjacent powder layer can also reduce residual stress (Cheng et al. 2016).

The underlying mechanisms of the scanning strategies to reduce residual stresses are explained as follows. The largest planar stress component generated is parallel to the scan vector, and it increases with the scan vector length. Through a coupled

thermo-mechanical simulation, the longitudinal stress (parallel to the scan vector) increases with the scan vector length, and it is the main contributor to residual stress due to the presence of a larger thermal gradient parallel to the scan vector (Parry et al. 2016). Additionally, residual stress and plastic strain are reduced at the end of scan vectors when using the alternate scanning strategy because of the reduced temperature gradients at the end of each vector. Based on these findings, the designed scanning strategies should avoid long scan vector lengths and instead emphasize on orientating the direction of scan vectors uniformly to produce an isotropic stress field in the component.

The effects of laser power, scanning speed, and layer thickness on the residual stress of LPBF-printed Inconel 718 thin-walled parts have been investigated (Chen et al. 2019a). In the study, the residual stress in an LPBF-printed Inconel part was observed to increase with an increase in laser power from 250 to 450 W, and its maximum von Mises stress increased by 22%. The residual stress decreased with an increase in scanning speed from 500 to 1000 mm/s, and the maximum von Mises stress decreased by 14%. The residual stress decreased with an increase in layer thickness from 20 to 60 μm , and the maximum von Mises stress was reduced by 33%. As shown in Figure 3.20, the nature of the residual stress changed from compressive to tensile along the deposition direction, and its magnitude increased with the deposition height. The maximum stress occurred at both ends of the interface between the part and substrate, while the second-largest stress occurred near the top center of the part.

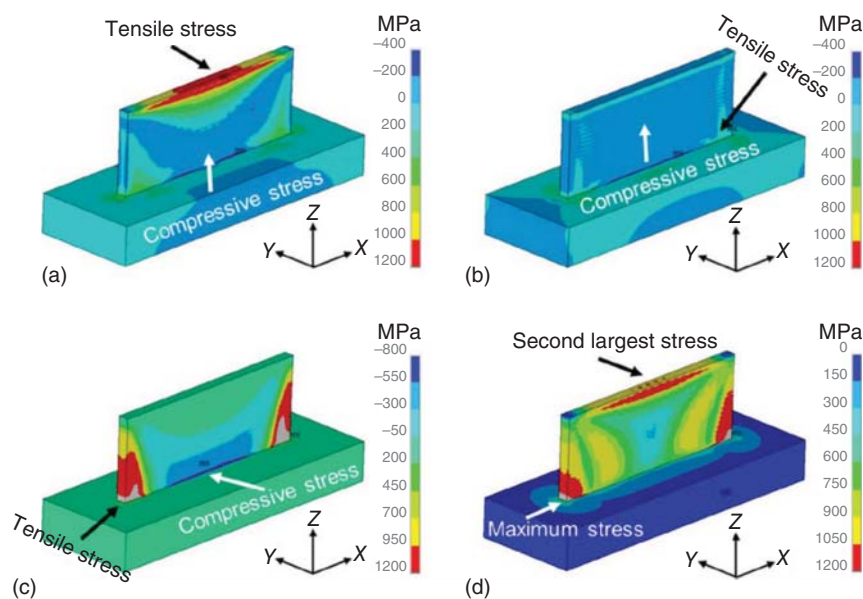


Figure 3.20 Stress distribution in a thin-walled part. (a) X-component stress, (b) Y-component stress, (c) Z-component stress, and (d) von Mises stress. Source: Reproduced from Chen et al. (2019a)/with permission from Emerald Publishing Limited.

The residual stress of LPBF-printed parts can be measured through destructive testing methods, including microhardness testing and the contour method, and non-destructive methods such as X-ray diffraction (XRD) and neutron diffraction.

For alloys without significant precipitates and dominated by a single matrix phase, the shape of their microhardness indents can be utilized to quantify the residual stress. However, the microhardness only reveals information about the stresses near the tested surfaces.

Both XRD and neutron diffraction can be conducted to measure bulk stress variation. However, the two technologies are relatively expensive. They require specialized equipment, and the penetration depth of the radiation beams of both processes is limited, especially for bulky parts with constituent elements of high atomic numbers.

The contour method measures the deflection of the printed surfaces to obtain their residual stresses and can provide results comparable to those obtained by neutron diffraction. It was utilized to measure the residual stress of LPBF-printed Ti-6Al-4V along three orientations, as shown in Figure 3.21 (Vrancken et al. 2014b). The stress field in the XY sample exhibited tension at the center, which was balanced by compressive stresses at the left and right edges. In the XZ and ZX samples, there were compressive stresses at the center and tensile stresses near the top and bottom edges.

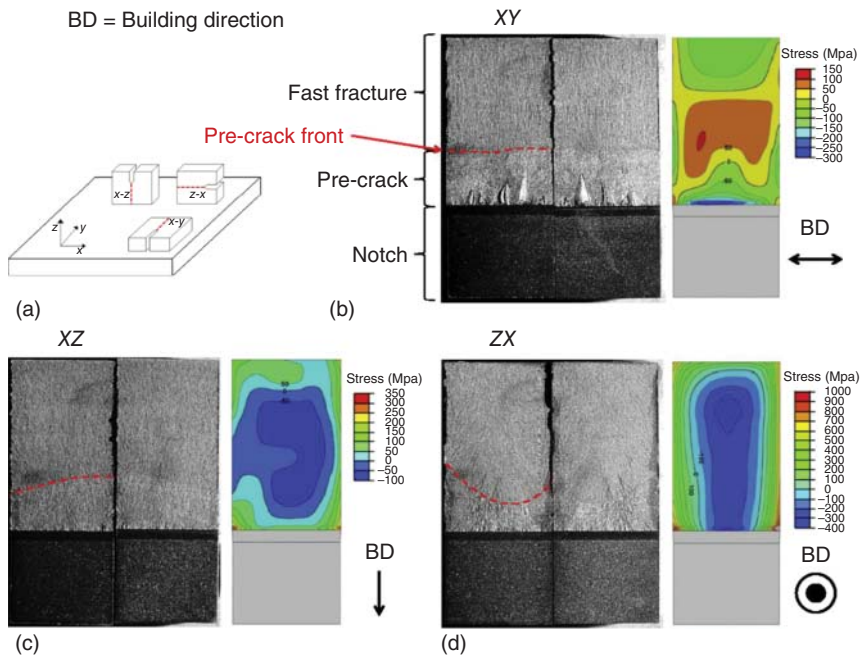


Figure 3.21 (a) Schematic illustration of the sample orientation for residual stress measurement. Representative residual stress plots of LPBF-printed Ti-6Al-4V along three orientations. (b) XY sample, (c) XZ sample, and (d) ZX sample. Source: Vrancken et al. (2014b)/reproduced with permission from Elsevier.

The residual stress distributions and magnitudes provided clear insight into the behavior of the material. The pre-crack fronts of the XY and XZ samples were both relatively straight. The residual stress of those samples was lower than their yield stress, as shown in Figure 3.21a,b. Moreover, at the notch where the pre-crack was initiated, the maximum and minimum stress differed by ~ 300 MPa. As the pre-crack grew, the residual stress distribution was readjusted, and the difference decreased. For the ZX sample, the maximum and minimum stress at the notched edge differed by >1 GPa. This result indicates that one part of the crack front may be experiencing tensile stress sufficiently high to cause crack growth, and the other parts experienced almost no stress or even compressive stress. The uneven stress distribution resulted in the crack propagating faster along the sides and led to the curved shape of the pre-crack front, as shown in Figure 3.21c.

Large residual stresses bring about great challenges to the design and manufacturing of LPBF parts. The residual stress-induced warpage is especially severe for overhanging regions printed without any support structures beneath them. Support structures are useful for overhanging features because they bear the weight of the feature and compensate for any distortion along the horizontal direction. Moreover, a support structure facilitates heat dissipation as the loose powder possesses poor thermal conductivity. It also provides additional material stock to the base plate for more precise part removal. Although support structures decrease residual stress values, stress-relieving heat treatment is still required (Mishurova et al. 2018).

Despite the advantages of support structures, it is difficult to remove them from internal structural features, such as cooling channels, since these structural features generally lack accessibility. Moreover, the removal of supports may incur additional post-processing and material costs and may cause potential damage to the parts.

For certain crack-prone materials, the presence of residual stress can accelerate the formation of cracks. It is widely accepted that the enrichment of low-melting-point alloy components and precipitates along grain boundaries can produce intergranular cracks with lengths of a few microns up to $100\text{ }\mu\text{m}$ and more. For example, the hot cracking mechanism aggravated by residual stress in an LPBF-printed nickel-based superalloy IN738LC was revealed (Cloots et al. 2016). During cooling, the emerging grains were oriented preferentially along the build direction, which is the direction in which rapid crystallization occurs the most. Because of the rapid solidification, the solidus temperature was lowered until a pronounced critical temperature range (CTR) was characterized, whose boundaries were described by the liquidus and solidus temperatures (Figure 3.22). However, the complete homogenization of the liquid alloy within the CTR was impossible.

Consequently, low-melting-point films with a high concentration of Zr, a product of constitutional undercooling, covered the emerging grains. This led to brittle grain boundaries, resulting in the grains being unable to transfer the residual tensile stress or accommodate the shrinkage caused by the cooling melt. Depending on the liquid film dimension and the strain at the grain boundary, a separation between two adjacent grains may occur, which is perceived as a solidification crack (scenario I in Figure 3.22). In addition, residual stress allows the preexisting solidification crack

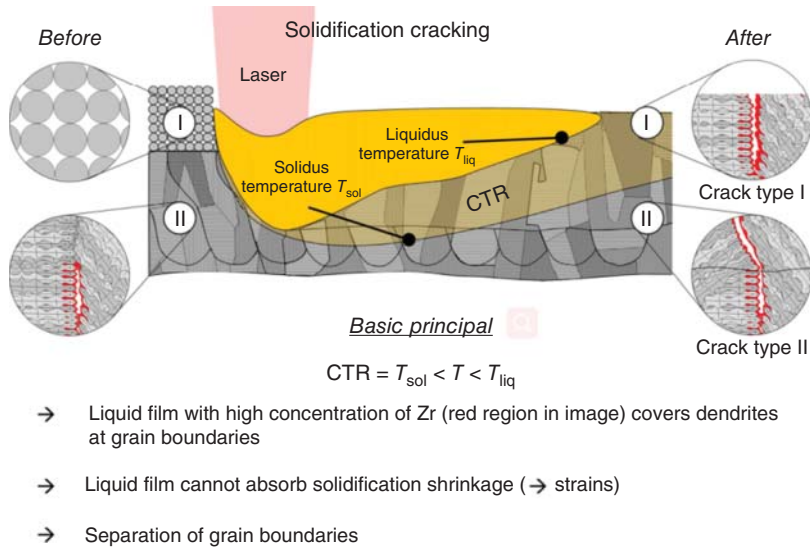


Figure 3.22 Schematic illustration of the solidification crack initiation in an LPBF-printed IN738LC alloy due to residual stress. Source: Reproduced from Cloots et al. (2016)/with permission from Elsevier.

to serve as a nucleus for continuous crack growth in the subsequent layers, as illustrated in scenario II.

In general, residual stress is undesirable since it results in shape distortion of the printed parts. Residual stress and warpage of LPBF-printed parts can be reduced by (i) applying stress-relief heat treatment, (ii) rescanning with lower laser energy densities to effectively stop crack propagation, (iii) preheating substrates to lower the temperature gradient, and (iv) shortening melt tracks with the island/checkerboard scanning strategy and scanning with a rotating scan pattern. However, retaining a reasonable residual stress level in LPBF-printed parts may enhance their hardness (Gu and Meiners 2010), demonstrating that residual stress is not always detrimental to part quality and may be beneficial depending on the applications.

3.5 Powder Materials

Powder quality is one of the critical factors determining the quality of LPBF parts. Poor powder quality can produce defects in the final part, including pores, cracks, inclusions, residual stress, and suboptimal surface roughness, which compromises the throughput. Powder characteristics are governed by the morphology, particle size, surface chemistry, moisture, packing density, and rheological and thermal properties, which affect feedstock behavior and subsequent printing processes. In general, smooth flowability and high powder packing density are desirable to ensure successful material deposition and part densification during the LPBF process.

Powder particles produced from different atomization techniques exhibit various particle morphologies and sizes, as discussed in Chapter 2. Highly spherical particles are often desired in the LPBF process because of their high powder packing density and rheological performance. Hence, qualified powder typically consists of primarily spherical particles with few irregularly shaped or angular grains. Given the same particle size distribution, spherical particles pack more efficiently than irregular particles, resulting in higher packing densities.

In addition to powder morphology, particle size distribution is commonly utilized to quantify powder particle sizes in terms of their volume composition. The particle size distribution fluctuates over various stages of the LPBF process, such as powder storage, spreading, and recycling, thus inducing variations in the feedstock behavior. Powder coarsening can result from pre-sintering of the particles near the melting zone, at which droplets of molten metal ejected from melt pools may adhere to unfused particles, forming larger and less spherical powder particles. The increase in powder aggregation with a higher number of build cycles disrupts the flow and packing performance of the recycled powder for subsequent printing operations. Therefore, before using the used feedstock, necessary sieving procedures are performed during powder recycling operations to minimize size deviations from the original particle distribution array.

The study of granulometry variation has gained traction in the LPBF process and other powder-based AM techniques as changes in powder size can influence material processability throughout the printing process. A typical powder particle size distribution of powder used for LPBF is 10–45 μm , which aims to achieve high part density and surface quality under available laser energy densities (Spierings et al. 2011). However, a slight deviation from the above range of 20–63 μm is also acceptable in some cases.

Fine particles smaller than 10 μm are not preferred as they can contribute to poor powder flowability. As the percentage of fine powder particles increases (corresponding to finer average particle size), the Carney flow time begins to increase until no flow occurs, which can be attributed to increased friction between particles and agglomeration due to static charge. Moreover, fine powder particles are an inhalation hazard. Therefore, the volume percentage of powder particles smaller than 10 μm should be limited in real applications.

Powder contamination is an underlying issue with LPBF, especially during the processing of highly reactive feedstocks, such as magnesium, titanium, and aluminum alloys. Contaminant levels of just a few parts per million can significantly affect the final part quality. The prolonged exposure of reactive feedstock to external environments, interstitial gas intrusions, and the proximity to heat irradiation during part forming may trigger oxidation reactions (Starr et al. 2012). In addition, the drop in water vapor pressure at elevated build chamber temperatures can trigger the formation of hydroxide layers to produce oxides upon crystallization.

Although the LPBF process is often performed under a controlled inert atmosphere in which O_2 concentrations are much lower than 0.15%, oxygen pickup and inclusion are unavoidable, especially in chemically reactive powder materials (Strondl et al. 2015). The oxygen content of recycled Ti–6Al–4V powder was

observed to rise above 50% of its original composition, which resulted in a 14% decrease in overall part toughness. Additionally, the reduction in ductility was also accompanied by an increase in part porosity from 0.17% to 0.36% following powder re-usage, which was caused by decreased powder flowability due to changes in the particle shape.

The addition of inhibitors to curb oxidation issues, such as phosphorus and carbon, has been reported to provide deoxidizing effects, which helped reduce the surface tension of melt pools, thereby preventing balling in Fe-based alloys (Kruth et al. 2004). Deoxidizing treatment methods can also be integrated into powder recycling solutions to retain the recycled feedstock quality.

If moisture is adsorbed onto the surface of a powder, its flow behavior may be adversely affected. For alloys susceptible to oxygen and hydrogen pickup, such as titanium and aluminum, the decomposition of hydrogen and oxygen from the water vapor during melting may increase these elements in the resultant solution. Irradiation contact with adsorbed water layers also facilitates the dissociation of hydrogen atoms from water molecules during laser–powder interaction, which can produce entrapped gas pores upon melt pool solidification, thereby resulting in melt pool spattering. Moisture adsorption on the powder surface can contribute to slow-flowing powder due to polarity effects. Depending on the situation, it may be helpful to heat a powder at low temperatures or under a vacuum to improve its flowability. The drying step can aid in the removal of residual moisture from used powder.

The powder materials for LPBF can be classified into pure metals, pre-alloys, and multicomponent mixed metals/alloys (Gu et al. 2012a). Pre-alloyed powders are usually produced through atomization processes, and multicomponent mixed powders can be obtained through mechanical alloying or blending. LPBF can be used to print a broad spectrum of metal powder materials, including Fe-based alloys, Ti-based alloys, Al-based alloys, Ni-based alloys, Co-based alloys, Cu-based alloys, high-entropy alloys (HEAs), metallic glass alloys, and their composites, which are commonly employed in various industrial applications. A summary of these materials amenable to LPBF is provided in Table 3.1, although it may not be exhaustive due to active ongoing research in the LPBF community.

The powder particle shape, size, and size distribution strongly influence laser absorption, powder spreading, powder bed density, and powder bed thermal conductivity. Finer powder particles provide a greater specific surface area and absorb laser energy more efficiently than coarser particles. Powder bed densities typically range between 50% and 60% for most commercially available powders. Generally, a higher powder packing density corresponds to a higher powder bed thermal conductivity and better mechanical properties of parts. The typical effects of powder granulometry on 316L powder performance for LPBF and the final part performance are presented in Table 3.2.

During the powder spreading process, three dominant kinds of deposition mechanisms have been identified: the wall effect, percolation effect, and cohesion effect, which compete with each other during the spreading process and cumulatively affect the packing density of the powder layer, as shown in Figure 3.23 (Chen et al. 2019b).

Table 3.1 Summary of metal powder materials amenable to LPBF.

Materials	Commercial equivalents
Titanium	Commercially pure Ti, Ti-6Al-4V, Ti-6Al-4V ELI, Ti-6Al-7Nb, Ti-24Nb-4Zr-8Sn, Ti-13Zr-Nb, Ti-13Nb-13Zr, Ti-Nb, Ti-Ta, Ti-Nb-Ta, Ti-5.5Al-3.4Sn-3Zr, TiAl
Iron	Pure Fe, 316L, 304L, 314S, M2, H13, 17-4 PH, H20, 15-5 PH, Inox904L, AISI Maraging 300, X110CrMoVAl 8-2, GP1, Fe-Ni, Fe-Ni-Cu-P, Fe-Ni-Cr, Fe-Al, Fe-Cr-Al, ultrahigh carbon steel, EH36
Aluminum	Pure Al, Al-Si10-Mg, Al-Si-7Mg, AlSi12, AlSi20, AlSi50, Al-20Si-5Fe-3Cu, Al-Zn-Mg-Cu, Al-Cu-Mg, Al6061, Al7075, Al2024, Al2195, Al2219, Al2618, Al4047, ScalmalloyRP
Nickel	Inconel 718, Inconel 625, Chromel, Hastelloy X, IN738LC, Nimonic 263, MAR-M 247, NiTi
Cobalt	Co-Cr-Mo, Co-Cr-W, Stellite 21
Copper	Pure Cu, Cu-9Al, Cu-10Sn, Cu-Ni, K220, C18400, NiAl bronze, Brass
Tantalum	Pure Ta
Molybdenum	Pure Mo
Magnesium	Pure Mg, AZ31, AZ91D, ZK60, Mg-9Al, WE43, Mg-Mn
Tungsten	Pure W, 80W-20Fe, 90W-7Ni-3Fe, W-6Ta
Zirconium	Pure Zr
Zinc	Pure Zn
Gold	Pure Au, 3N (18k), 24 Karat gold
Silver	Pure Ag, Sterling silver
High-entropy alloys	CoCrFeMnNi, AlCoCrFeNi, CoCrFeNi, CoCrFeNiTi, CoCrFeNiC, AlCrFeNiV, AlCrCuFeNi, NiCrWFeTi, AlCoFeNiSmTiVZr, MoNbTaW
Metallic glass alloys	Fe-based, Zr-based, Ti-based, Ti/Zr-based

The wall effect can reduce the packing density of the powder layer and is categorized into static and dynamic wall effects. The static wall effect emerges when a stress dip exists at the bottom of the moving powder pile during the powder spreading process, forcing the powder layer to be uniformly deposited regardless of the powder pile size variation along the rake and spreading directions. In addition to the static wall effect of the rake and baseplate, the force-arches act as dynamic walls. The static and dynamic wall effects lead to more voids in the powder layer, thereby causing the packing density of the thin powder layer to be lower than those of powder heaps packed in large containers. This phenomenon becomes more prominent with a decrease in layer thickness or an increase in particle size. The percolation effect exists in bimodal powder particles, which leads to particle segregation within the powder layer, thus reducing the packing density. Therefore, although using bimodal

Table 3.2 Effects of powder granulometry on the performance of LPBF-printed 316L parts. Note that grade herein refers to the classification of the powder size distribution.

Performance	Key findings
Part density	• A negatively skewed powder containing fine particles led to higher part densities than a finer Gaussian grade at a lower layer thickness^{a)} • The use of powders with fine granulometry can provide better densification of parts than coarse grades^{a)} • Finer particles tend to vaporize at low speed and high energy density, resulting in keyhole porosities^{b)} • The more efficient packing behavior of multimodal powders contributed to high part densification compared to Gaussian powders^{c)}
Mechanical properties	• The negatively skewed grades exhibited high ductility but low tensile strength as compared to powders with a Gaussian size distribution^{d)} • The presence of fine particles induced rapid melting and a prolonged melt pool life, producing coarse grains that reduced the strength of the printed part^{d)} • Powder with a narrower size distribution exhibited higher mechanical strength but smaller elongation of the printed part as compared to the powder with a broader size distribution^{e)}
Surface quality	• Powders with fine granulometry generated better surface quality over coarser grades; more widely distributed powder (0–45 μm) exhibited better side surface roughness than narrower grades (10–45 μm)^{f)} • A positively skewed powder with a higher composition of fine particles generated a smoother melt pool surface than a negatively skewed powder of a similar particle size range^{g)}

a) (Spierings and Levy 2009);
b) (Liu et al. 2011);
c) (Olanmi et al. 2012);
d) (Spierings et al. 2011);
e) (Liu et al. 2011);
f) (Spierings et al. 2011);
g) (Lee and Zhang 2015).

powders improves the packing density for large volumes of powder particles, it is not necessarily applicable to the thin powder layer in LPBF. The cohesion effect caused by the van der Waals force can be estimated by the bonding number K . This effect leads to particle agglomeration, reduces the packing density, and becomes more prominent with a decrease in particle size.

3.6 Equipment

A typical LPBF equipment setup comprises an optical system, an elevator system, a recoating system, an air circulation system, and software and control systems. The optical system is the core module in LPBF equipment.

Lasers play a vital role in the LPBF technique and its equipment development. Of the many laser sources discovered over the years, carbon dioxide and Nd:YAG lasers

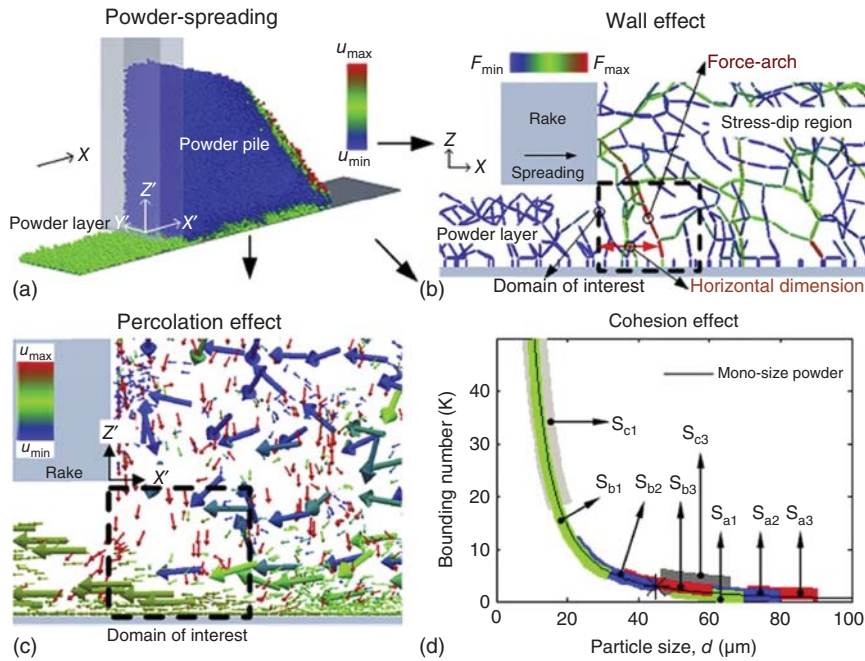


Figure 3.23 Fundamental mechanisms of powder spreading in LPBF revealed through the discrete element method. (a) Velocity field u of the powder pile during the powder spreading process. (b, c) Close-up views of the region near the bottom of the powder pile illustrating the dynamic wall effect and percolation effect. The lines in (b) refer to the magnitude of the contact forces F between neighboring powder particles. (d) Illustration of the cohesion effect, where $S_{a,b,c}$ denote different powder samples with different size distributions. Source: Reproduced from Chen et al. (2019b)/with permission from Elsevier.

have dominated metal AM from the late 1980s to the early 2000s. Afterward, fiber, disk, and diode lasers have become the lasers of choice for simplifying and improving the process (Dutta Majumdar and Manna 2011). A fiber, diode, or disk laser with a wavelength of $\sim 1 \mu\text{m}$ is more efficient than a CO_2 laser with a wavelength of $\sim 10 \mu\text{m}$ because of the greater laser absorptivity of the metal at shorter wavelengths.

Laser output power, spatial distribution, time dependence (pulsed or continuous), beam diameter, and beam divergence affect the rate at which energy can be delivered to the material and the spatial distribution of energy. Wavelength is a key factor in determining the suitability of a laser for a particular application. A correct wavelength must be chosen at which the selected material can absorb the energy, or else there will be no transfer of energy into the material. Consequently, no heating or state variation will occur (Figure 3.2). The angle of incidence of the beam to the material and its polarization characteristics determine how much of the incident laser light is reflected from its surface. The spatial distribution of the laser beam on the surface of a material affects the maximum irradiance obtained and the resultant temperature distribution. A Gaussian laser beam with the maximum intensity at its center is usually employed in LPBF. Therefore, the temperature of a

produced melt pool surface is higher at the center than at its boundary, producing a radial temperature gradient. This temperature gradient implies a surface tension gradient, which drives the surface profile and mass flow in a melt pool through the Marangoni flow. Most commercialized LPBF manufacturers use continuous-wave lasers. However, a pulsed laser can form a flat melt pool, thereby reducing the tendency of the balling phenomenon.

Additionally, the optical system consists of a scanner, a collimator, beam expander optics, and optical fiber. The optical fiber from the laser is connected to a collimator (a device for aligning beams), which is fastened to the beam expander optics with a holder and protected with a cover. The beam expander optics shape the laser beam propagating from the collimator and define how it reaches the scanner and its related focusing capability. The scanner has a significant impact on the part's accuracy. It guides the laser beam from the beam expander optics along a defined path over the building area using two mirrors operated by galvanometers. An integrated autocalibration feature checks the mirror positions and regulates the positions to reduce offset and gain drift. The laser beam is focused on the building area by an F-theta module.

The recoating system comprises a linear axis with a stepper motor and a recoater with a blade or roller installed in the chamber. The stepper motor moves the recoater in the x - y plane, uniformly distributing the metal powder onto the printing area.

In general, both soft and hard recoaters are commonly employed. A soft recoater possesses blades made from silicone, rubber, or soft carbon fiber, which can deform slightly from a collision due to their flexibility. This type of recoater is ideal for printing different parts on the same build platform; even if one of the parts is deformed or is built inaccurately, the other parts will continue to be produced, and the printing process does not have to be stopped. A hard recoater has blades made of high-speed steel or ceramic, which exert pressure on the powder and do not offer much tolerance for part deformation compared to the soft recoater. When the hard recoater collides with a part, the printing process stops promptly to prevent solidified segments of the part from being dragged across the powder bed. If one of the parts is deformed or is not built successfully, it may be preferable to stop the printing process to prevent a collision. Achieving a uniform powder thickness in each layer is essential to control the quality of the part built on the powder bed. A sufficient amount of powder for building each layer is supplied by dropping a controlled powder volume through a recoater. A powder delivery system should maximize the powder's flowability and minimize the formation of a particle cloud and the shear forces over the previous layer of the build.

The elevator system consists of building, dispensing, and collecting subsystems, of which each subsystem contains a platform mounted in a duct with a linear guide. During the building process, the building system lowers the building platform by the thickness of a single layer after each exposure. Once the building process is completed, the operator can move the building platform with the completed part to the home position. The dispenser platform conveys the metal powder required for the building process from the dispenser duct to the process chamber. In the collecting system, excess metal powder falls onto the collector platform in the collector duct. The operator can elevate the collector platform and push the excess metal powder into the dispenser duct to be reused.

The air circulation system ensures that the process chamber is filled with an inert gas to prevent the metal powder from oxidizing. In the inert gas cylinder, injection nozzles produce a continuous flow of inert gas that removes metal vapor, liquid droplets from spattering, and dust from the inert gas atmosphere. The inert gas is extracted via an extraction nozzle or groove and fed to the recirculating filter unit for purification. The gas flow keeps the protective glass window free of the process by-products detrimental to process reliability.

The software and control systems use a large number of sensors to monitor the temperatures of the chamber and build platform, the status of the laser and scanning system, cooling system, electrical system, powder bed, melt pool, level of oxygen, gas flow, humidity, etc., thereby ensuring the regular operation of the aforementioned systems.

A variety of mature commercial LPBF equipment manufacturers have emerged all over the world, such as EOS (Germany), SLM Solutions (Germany), GE Additive (USA), 3D Systems (USA), Velo3D (USA), Renishaw (UK), Bright Laser Technologies (China), and Farsoon Technologies (China). A non-exhaustive list of the equipment developed by representative LPBF manufacturers and their available materials is summarized in Tables 3.3 and 3.4.

The development of LPBF equipment aims to increase productivity, improve process stability and part quality, reduce cost and time, print at a large scale, and implement part multifunctionality. For example, SLM Solutions has developed the NXG XII 600 machine equipped with twelve 1000 W lasers for high-volume production. It is up to 20 times faster than a standard single-laser system and 5 times faster than a quad-laser machine, with a building rate of 1000 cm³/h and an unrivaled output of 10 000 kg of parts produced per year. Additionally, the equipment enables the fabrication of short-range overhangs without supports down to an angle of 5° and long-range overhangs of several centimeters down to 10°. Similarly, the Sapphire® System developed by Velo3D can achieve angles as small as 10°, enabling support-free geometries and significantly less post-processing.

LPBF equipment can incorporate preheating modules for substrates, typically up to a temperature of 200 °C. Note that the TruPrint 5000 (Trumpf) and FormUp™ 350 (AddUp) systems can preheat up to 500 °C, and that the AconityMIDI (Aconity3D) even possesses high-temperature preheating of up to 1200 °C. According to Table 3.3, parts with a length greater than 500 mm can be printed via certain LPBF equipment developed for large-scale production, such as SLM®500 and SLM®800 (SLM Solutions), X LINE 2000R (GE Additive), BLT-S510/S600/S800 and BLT-C600/C1000 (Bright Laser Technologies), EP-M650 (E-Plus-3D), and DiMetal-500 (Laseradd). Hybrid additive and subtractive manufacturing equipment (OPM250L and OPM350L) is predominantly developed by Sodick.

3.7 Typical Materials Used in LPBF

3.7.1 Titanium and Its Alloys

Titanium and its alloys are widely employed in the chemical, aerospace, and biomedical industries due to their high strength-to-weight ratio, excellent biocompatibility

Table 3.3 Summary of typical commercialized equipment for LPBF.

Company	Equipment	Building volume (mm ³)	Laser power (W)	Scanning speed (m/s)	Focus diameter (μm)
EOS (Germany)	M 100	Ø 100 × 95	200	7	40
	M 290	250 × 250 × 325	400		100
	M 300-4	300 × 300 × 400	400 (4 lasers)		100
	M 400	400 × 400 × 400	1000		90
	M 400-4	400 × 400 × 400	400 (4 lasers)		100
SLM Solutions (Germany)	SLM®125	125 × 125 × 125	400	10	70–100
	SLM®280	280 × 280 × 365	400/700/ 700 + 1000		80–115
	SLM®500	500 × 280 × 365	400/700		80–115
	SLM®800	500 × 280 × 800	400/700		80–115
	NXG XII 600	600 × 600 × 600	1000 (12 lasers)	—	160
Trumpf (Germany)	TruPrint 1000	Ø 100 × 100	200 (2 lasers)	—	30–55
	TruPrint 3000	Ø 300 × 400	500	—	100–500
	TruPrint 5000	Ø 300 × 400	500 (3 lasers)	—	100–500
DMG Mori (Germany)	LASERTEC 12 SLM	125 × 125 × 200	200/400	—	35
	LASERTEC 30 SLM 2nd Gen	300 × 300 × 300	600/1000	—	70–200
Aconity3D (Germany)	AconityONE	Ø 400 × 400	400 (4 lasers)/1000	4	80–500
	AconityMIDI	Ø 170 × 250	400 (2 lasers)/1000		80–500
GE Additive (USA)	Mlab cusing/Mlab cusing R	50 × 50 × 80; 70 × 70 × 80; 90 × 90 × 80	100	7	50
	Mlab cusing 200R	100 × 100 × 100	200		75
	M2 cusing/M2 cusing Multilaser	250 × 250 × 350	400 (2 lasers)		50
	X LINE 2000R	800 × 400 × 500	1000 (2 lasers)		100–500

Table 3.3 (Continued)

Company	Equipment	Building volume (mm ³)	Laser power (W)	Scanning speed (m/s)	Focus diameter (μm)
3D Systems (USA)	DMP Flex 100	100 × 100 × 80	100	—	—
	ProX® DMP 200	140 × 140 × 100	300	—	—
	ProX® DMP 300	250 × 250 × 300	500	—	—
	DMP Flex 350	275 × 275 × 380	500	—	—
	DMP Factory 350	275 × 275 × 420	500	—	—
Velo3D (USA)	Sapphire® System	Ø 315 × 400	1000 (2 lasers)	—	—
Renishaw (UK)	AM 400	250 × 250 × 300	400	—	70
	RenAM 500M	250 × 250 × 350	500	—	—
	RenAM 500S/500Q	250 × 250 × 350	500 (4 lasers)	10	80
Bright Laser Technologies (China)	BLT-S210	105 × 105 × 200	500	7	—
	BLT-S310/S320	250 × 250 × 400	500 (2 lasers)	—	—
	BLT-S400	400 × 250 × 400	500 (2 lasers)	—	—
	BLT-S450	400 × 400 × 500	500 (4 lasers)	—	—
	BLT-S510	500 × 500 × 1000	500 (4 lasers)	—	—
	BLT-S600	600 × 600 × 600	500 (4 lasers)	—	—
	BLT-S800	800 × 800 × 600	500 (6 lasers)	—	—
	BLT-A160/A160D	160 × 160 × 100	200 (2 lasers)	—	—
	BLT-A300/A320	250 × 250 × 300	500 (2 lasers)	—	—
	BLT-C600	600 × 600 × 1000	1000/2000/4000	—	—
	BLT-C1000	1500 × 1000 × 1000	2000/4000/6000	—	—
Farsoon Technologies (China)	FS121M	120 × 120 × 100	200	15.2	40–100
	FS271M	275 × 275 × 340	500	15.2	70–200
	FS301M	305 × 305 × 400	500 (2 lasers)	15.2	75–200
	FS421M	425 × 425 × 420	500 (2 lasers)	10	70–200

Table 3.3 (Continued)

Company	Equipment	Building volume (mm ³)	Laser power (W)	Scanning speed (m/s)	Focus diameter (μm)
E-Plus-3D (China)	EP-M150T	Ø 150 × 80	200	8	40–60
	EP-M150Pro	Ø 150 × 240	200/500 (2 lasers)		60
	EP-M150	Ø 150 × 120	200/500 (2 lasers)		40–60
	EP-M250	250 × 250 × 300	200/500		—
	EP-M250Pro	262 × 262 × 350	500 (2 lasers)		70
	EP-M260	266 × 266 × 390	500/1000 (2 lasers)		70–100
	EP-M300	305 × 305 × 450	500/1000 (2 lasers)		90–130
	EP-M450	455 × 455 × 500	500 (2 lasers)		80–120
	EP-M650	655 × 655 × 800	500 (4 lasers)		80–120
Laseradd (China)	DiMetal-50	50 × 50 × 50	70	7	20
	DiMetal-300	250 × 250 × 300	500		—
	DiMetal-500	500 × 250 × 300	500 (2 lasers)		—
Sisma (Italy)	MYSINT 100	Ø 100 × 100	200	—	55
	MYSINT 100 RM Dual laser	Ø 100 × 100	200 (2 lasers)	—	55
	MYSINT 300	Ø 300 × 400	500	—	100–500
AddUp (France)	FormUp™ 350	350 × 350 × 350	500 (2 lasers)	10	—
Matsuura (Japan)	LUMEX Avance-25	256 × 256 × 300	500/1000	—	—
	LUMEX Avance-60	600 × 600 × 500	1000	—	—
Aurora Labs (Australia)	S-Titanium Pro	200 × 200 × 250	300	—	—
	RMP1	Ø 450 × 400	—	—	—
Sodick (Japan)	OPM250L	250 × 250 × 250	500	—	—
	OPM350L	350 × 350 × 350	500	—	—

Table 3.4 Summary of available powders for the commercialized LPBF equipment.

Company	Available powders
EOS (Germany)	● M 100: CoCr, 316L, Ti-6Al-4V, W ● M 290: Al-Si10-Mg, CoCr, Maraging steel, IN625, IN718, 316L, 17-4 PH, Ti-6Al-4V, Ti-6Al-4V ELI, CP Ti ● M 300-4, M 400: IN718, Maraging steel, Ti-6Al-4V, Al-Si10-Mg ● M 400-4: Al-Si10-Mg, Maraging steel, IN718, 316L, Ti-6Al-4V, CP Ti, Ti-6Al-4V ELI
SLM Solutions (Germany)	Al-Si10-Mg, AlSi7Mg0.6, AlSi9Cu3, Ti-6Al-4V ELI, TA15, CP Ti, IN625, IN 718, IN939, Ni-Cr-Fe, 316L, 15-5 PH, 17-4 PH, H13, Invar 36, Co-Cr-Mo, CuNi10, CuNi2SiCr
Trumpf (Germany)	AlSi9Cu3, Al-Si10-Mg, AlSi12, 316L, 630, CoCr, bronze, IN625, IN718, Ti2, Ti-6Al-4V, tool steel
DMG Mori (Germany)	Ti-6Al-4V, Al-Si10-Mg0.5, Co-Cr-Mo, 316L, 17-4 PH, IN625, IN718, IN738, tool steel, CM 24 LC
Aconity3D (Germany)	316L, 17-4 PH, maraging steel, 15-5 PH, H13, Hastelloy X, IN625, IN718, IN939, AlSi9Cu3, AlSi12, AlSi7Mg, Al-Si10-Mg, Ti-6Al-4V, Ti6Al7Nb, CP Ti, CoCr
GE Additive (USA)	● Mlab cusing/Mlab cusing R: 316L, Al-Si10-Mg, Ti-6Al-4V ELI, CP Ti, bronze, 17-4 PH, CoCr, 18 karat 3N, 18 karat 4N, 18 karat 5N, Pt alloy, Ag alloy ● Mlab cusing 200R: 316L, Al-Si10-Mg, Ti-6Al-4V ELI, CP Ti, bronze, 17-4 PH, IN718, maraging steel, CoCr ● M2 cusing/M2 cusing Multilaser: 316L, Al-Si10-Mg, F357, Ti-6Al-4V ELI, CP Ti, hot-work steel, bronze, 17-4 PH, IN718, IN625, CoCr ● X LINE 2000R: Al-Si10-Mg, Ti-6Al-4V ELI, IN718
3D Systems (USA)	● DMP Flex 100: CoCr, 17-4 PH, 316L ● ProX® DMP 200: CoCr, 17-4 PH, maraging steel, AlSi12, 316L, IN625 ● ProX® DMP 300: CoCr, 17-4 PH, maraging steel, AlSi12 ● DMP Flex 350, DMP Factory 350: CoCr, 17-4 PH, maraging steel, AlSi12, AlSi7Mg0.6, Al-Si10-Mg, CP Ti, Ti alloys, IN625, IN718, 316L

Table 3.4 (Continued)

Company	Available powders
Velo3D (USA)	IN718, Ti-6Al-4V
Renishaw (UK)	Ti-6Al-4V ELI, Al-Si10-Mg, CoCr, 316L, IN625, IN718, maraging steel
Bright Laser Technologies (China)	● BLT-S210: Ti alloy, Al alloy, high-temperature alloy, CoCr, stainless steel, high-strength steel, tool steel, Cu alloy, W alloy, Mg alloy, Ta ● BLT-S310/S320, BLT-S400, BLT-A300/A320: Ti alloy, Al alloy, high-temperature alloy, stainless steel, high-strength steel, tool steel, Cu alloy ● BLT-S450, BLT-S4510, BLT-S600, BLT-S800, BLT-C600: Ti alloy, Al alloy, high-temperature alloy, stainless steel, high-strength steel, tool steel ● BLT-A160/A160D: CoCr, Ti alloy ● BLT-C1000: Ti alloy, high-temperature alloy, stainless steel, high-strength steel
Farsoon Technologies (China)	● FS121M: 316L, Co-Cr-Mo-W, Co-Cr-Mo, 17-4PH, CuSn10 ● FS271M: 316L, 17-4PH, 15-5PH, 420, Co-Cr-Mo-W, Co-Cr-Mo, Ti-6Al-4V, TA15, Al-Si10-Mg, 18Ni300, CuSn10, GH3536, IN718, IN625 ● FS301M: Al-Si10-Mg, Ti-6Al-4V, 316L ● FS421M: Al-Si10-Mg, Ti-6Al-4V, 316L, IN718, GH3536, TA15
E-Plus-3D (China)	● EP-M150T, EP-M150Pro, EP-M150, EP-M250: Ti alloy, CoCr ● EP-M250Pro, EP-M260, EP-M300, EP-M450: Ti alloy, Al alloy, Ni alloy, maraging steel, stainless steel, CoCr, Cu alloy ● EP-M650: Ti alloy, Al alloy, Ni alloy, die steel, stainless steel, Co-Cr-Mo
Laseradd (China)	316L, CoCr, Ti-6Al-4V, high-temperature alloys, precious alloys, die steel

Table 3.4 (Continued)

Company	Available powders
Sisma (Italy)	● MYSINT 100, MYSINT 100 RM Dual laser: Gold, silver, platinum, titanium alloys, bronze, steel alloys, nickel alloys, CoCr ● MYSINT 300: Titanium alloys, aluminum alloys, steel alloys, nickel alloys, CoCr
AddUp (France)	Ti-6Al-4V, Al-Si10-Mg, 316L, 18Ni300, IN625, IN718
Matsuura (Japan)	316L, 630, Ti-6Al-4V, maraging steel, CoCr, IN718, Al-Si10-Mg
Aurora Labs (Australia)	316L, 304, 309, bronze, CP Ti, Ti-6Al-4V, IN718, iron, NiSiB
Sodick (Japan)	Maraging steel, 420, 630, 316L, IN718

and corrosion resistance, and low density (Banerjee and Williams 2013). In addition, the great variety of alloy composition and related microstructure, and the allotrope of Ti render Ti-based alloys one of the most interesting materials for academia and industry.

When the other process parameters were kept constant, the microstructure of LPBF parts fabricated from commercially pure (CP) Ti depended on the laser scanning speed (Gu et al. 2012b). The phase constitutions and microstructural characteristics of pure Ti parts underwent successive changes by increasing the laser scanning speeds: relatively coarsened lath-shaped α (100 mm/s) $\rightarrow$ refined acicular-shaped martensitic α' (200 mm/s) $\rightarrow$ further refined zigzag-structured martensitic α' (300–400 mm/s), as shown in Figure 3.24. In another study, the microstructures exhibited a phase transformation from the β phase to relatively coarse plate-like α grains when the laser power and scanning speed were less than 100 W and 100 mm/s, respectively, which was attributed to the occurrence of energy thermalization (Attar et al. 2014). Upon increasing the laser scanning speed beyond 100 mm/s, thermal and kinetic undercooling increased, leading to the formation of refined α' from β .

Ti-6Al-4V primarily comprises a hexagonal close-packed α phase and a body-centered cubic (BCC) β phase at room temperature. During the LPBF process, the α phase transforms into the β phase when heated above the β -transus temperature, while the β phase transforms to the primary α phase at a low cooling rate or to a martensitic α' phase at a high cooling rate. The LPBF-printed Ti-6Al-4V alloy generally exhibited a fine-grained acicular α' martensitic structure, as shown in Figure 3.25 (Thijs et al. 2010). The elongated prior β grains larger than 100 μm indicated epitaxial growth in the build direction. An increased heat input led to a larger width of the melt track and coarser prior β grains. As the printing progressed, the Ti_3Al phase (α_2 phase) precipitates appeared during consecutive reheating to

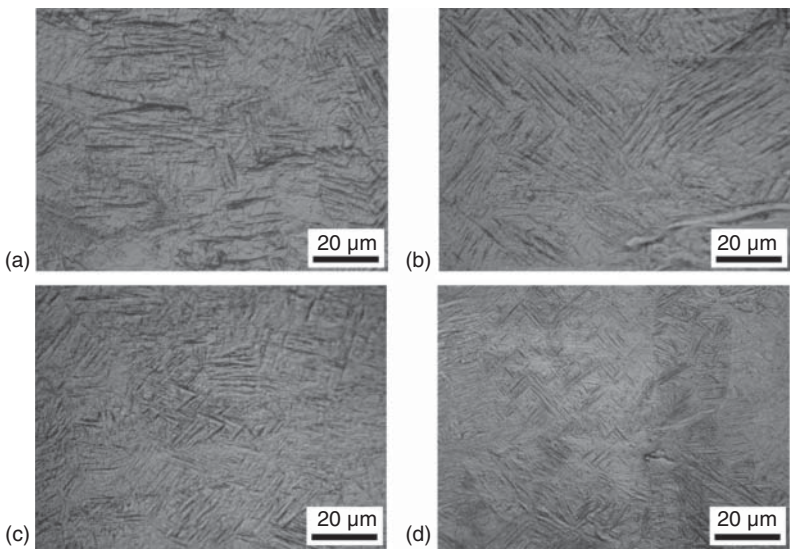


Figure 3.24 Microstructures of pure Ti dependent on LPBF process parameters. (a) Coarse lath-shaped α phase observed at a scanning speed of 100 mm/s, (b) refined acicular α' martensite at 200 mm/s, and (c, d) further refinement of the α' martensite at 300 and 400 mm/s, respectively. Source: Gu et al. (2012b)/reproduced with permission from Elsevier.

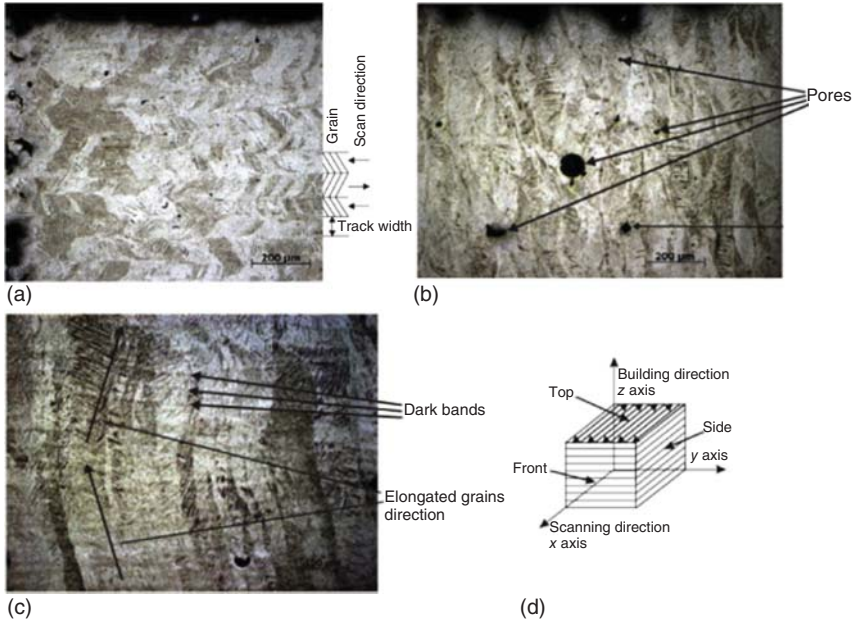


Figure 3.25 Microstructure of a Ti-6Al-4V alloy printed by LPBF. (a) Fine-grained herringbone structure corresponding to the scan direction, and (b) front and (c) side views of elongated prior β grains. (d) Schematic illustration of the sample orientation. Source: Thijs et al. (2010)/reproduced with permission from Elsevier.

500–600 °C. The high temperature gradients and short interaction time led to a small number of such precipitates. The lamellar spacing of the α phase decreased with the increase in cooling rate. Meanwhile, the α phase experienced *in situ* growth, and its amount depended on the local thermal cycles. Significant variation of the α phase lamellar spacing was observed in a single layer (Martina et al. 2012), which is a function of the peak temperature below the β transus. The thickness of the α phase at the grain boundary delineating the prior β grains depends on the cooling rate.

The Ti-6Al-4V sample fabricated under fast cooling conditions consists of acicular α' martensite that usually displays high yield strength but has limited ductility. Heat treatment is often required to transform the martensitic α' phase to $\alpha + \beta$ dual phases to achieve a compromise between strength and ductility. The width of the α lamella plate mainly depends on the heat treatment temperature. The prior β grains transformed to lamellar $\alpha + \beta$, α -Widmanstätten colonies, and α' martensite when subjected to furnace cooling, air cooling, and water quenching, respectively (Vrancken et al. 2012). The lamellar $\alpha + \beta$ and α -Widmanstätten colonies resulted in high ductility but low strength, while the α' martensite imparted high strength but low ductility. A previous study proposed a stress-relief treatment at 650 °C to form a very fine microstructure consisting of both α and α' phases (Wycisk et al. 2015). The thickness of an individual α -lamella was measured to be below 1 μm and slightly coarsened to $\sim 4 \mu\text{m}$ under HIP, as shown in Figure 3.26. Additionally, it was discovered that HIP conducted at 920 °C for four hours and a pressure of 103 MPa could

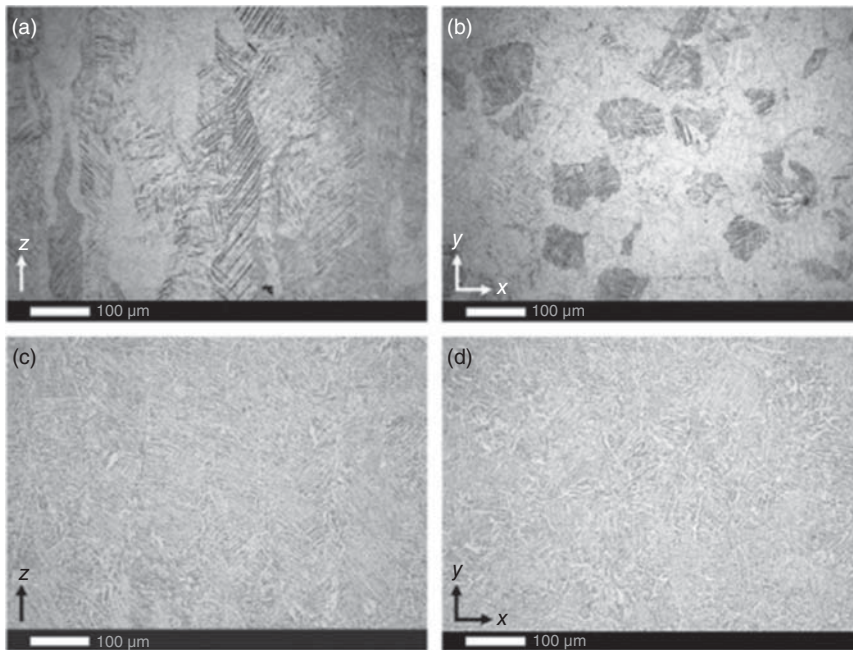


Figure 3.26 Microstructures of a Ti-6Al-4V alloy. (a, b) Stress-relieved condition after heat treatment at 650 °C for 3 h in a vacuum and (c, d) HIP condition. Source: Wycisk et al. (2015)/reproduced with permission from Frontiers Media S.A.

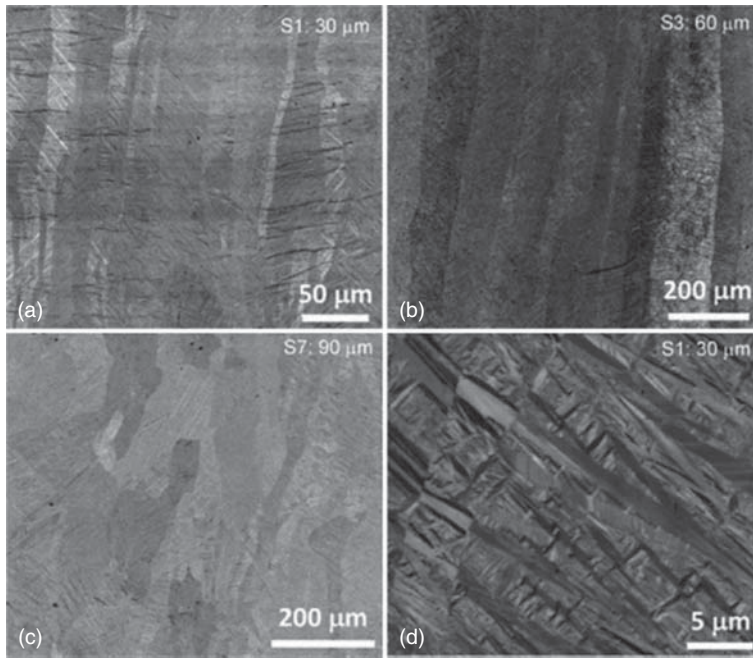


Figure 3.27 Effect of layer thickness on the microstructure of a Ti-6Al-4V alloy. (a) 30 μm , (b) 60 μm , and (c) 90 μm . (d) Magnification of the α' martensite phase shown in (a). Source: Xu et al. (2015)/reproduced with permission from Elsevier.

transform the as-printed martensitic α' microstructure into α and β phases with a simultaneous reduction in porosity (Qiu et al. 2013).

The type of deposition (single track or multilayer) and the LPBF process parameters, such as layer thickness, laser focal offset distance, and energy density, critically influence the microstructure of Ti-6Al-4V parts (Xu et al. 2015). Optimizing process parameters could decompose the brittle martensitic α' phase into a more ductile $\alpha + \beta$ microstructure, thus potentially avoiding the need for subsequent heat treatment. Columnar prior β grains were observed in all samples (Figure 3.27), and the α' martensitic phase was present at a layer thickness of 30 μm . However, the α' phase was found to decompose into an ultrafine lamellar $\alpha + \beta$ structure for layer thicknesses of 60 and 90 μm . This specific microstructure resulted from an *in situ* heat treatment at $\sim 400^\circ\text{C}$ induced by the buildup of consecutive layers. The top eight layers consisted of the α' phase regardless of the process parameters selected, as there were insufficient successive layers to reach the required temperature for decomposition.

Several investigations have focused on the direct relations between the mechanical properties of LPBF parts and the processing parameters or their microstructures. The most important parameters in determining the microstructures and the resulting properties are factors that influence the thermal history and cooling rates. Metallurgical defects, build location, and scanning strategies can directly affect the mechanical properties. The highest strength can be achieved if the

process conditions result in a very fine martensitic α' microstructure, which can be induced by the extremely high cooling rates of the LPBF process. According to the Hall–Petch relationship, grain refinement contributes to the increase in yield strength. The distorted hexagonal lattice structure of the α' martensite is more robust than that of the lamellar α due to its fine lath width, although it does not necessarily reduce the ductility. LPBF-printed Ti–6Al–4V has increased tensile strength compared to its cast or wrought counterparts. Conventionally processed Ti–6Al–4V with $\alpha + \beta$ phases exhibit a considerably lower elongation than pure Ti because of the blocking of the twinning deformation modes. With careful adjustment of the LPBF parameters, such as the layer thickness and volumetric energy density, the temperature cycle during the fabrication of parts may be controlled to allow for the decomposition of the α' martensite phase, leading to a favorable high strength and high ductility combination.

In situ fabrication via LPBF allows pure metals or powder particle reinforcements to be added to the titanium matrix to develop novel titanium alloys or titanium matrix composites, such as Ti/hydroxyapatite composites (Han et al. 2017a, 2018a), (TiB + TiC)/Ti composites (Han et al. 2020a), Mo_2C /Ti–6Al–4V composites (Cai et al. 2021b), Ti–Nb alloys (Zhao et al. 2020), and Ti–Ta alloys (Zhao et al. 2019, 2021). Notably, titanium matrix composites reinforced with TiB and TiC were fabricated *in situ* via LPBF (Han et al. 2020a). Varying contents of B_4C from 0 to 5 wt% were added to pure titanium to prepare blended powders for LPBF. The microstructure of the composite indicated that both the dendritic and cellular structures were arranged by coalescent clusters composed of TiB whiskers and TiC particles. In contrast, the clusters were formed through a self-joining phenomenon of the TiB whiskers that were mechanically locked with the TiC particles (Figure 3.28). The composites with the addition of 1 wt% B_4C exhibited the highest ultimate tensile strength of 946 MPa, yield strength of 762 MPa, and elastic modulus of 128 GPa, which were 62.4%, 49.2%, and 15.3% higher than those of the Ti matrix, respectively. The remarkable enhancement in mechanical strength was attributed to the synergistic effect of dispersion strengthening and grain refinement strengthening.

The microstructures can be tailored by the content of the additives, which has a profound effect on the mechanical properties. For example, the addition of 10 wt% Mo to Ti–6Al–4V completely suppressed the β to α' martensite transformation during rapid solidification by reducing the β -transus temperature from 995 to 900 °C. Thus, a combination of high strength and good ductility was achieved through the microstructure of a fully β -Ti matrix with dispersed Mo particles (Vrancken et al. 2014a).

Titanium–tantalum (Ti–Ta) alloys are endowed with the excellent mechanical properties of Ti and the osseointegration ability of Ta, and they have emerged as an attractive candidate for bone substitute materials. The role of Ta on the phase transformation, microstructure evolution, mechanical properties, and corrosion resistance of Ti–Ta alloys *in situ* manufactured via LPBF has been studied (Zhao et al. 2019). The results indicated that as the Ta content increased, martensite transformation was gradually suppressed in the printed Ti–Ta alloys due to the β stabilization effect of Ta. Furthermore, with increasing Ta content,

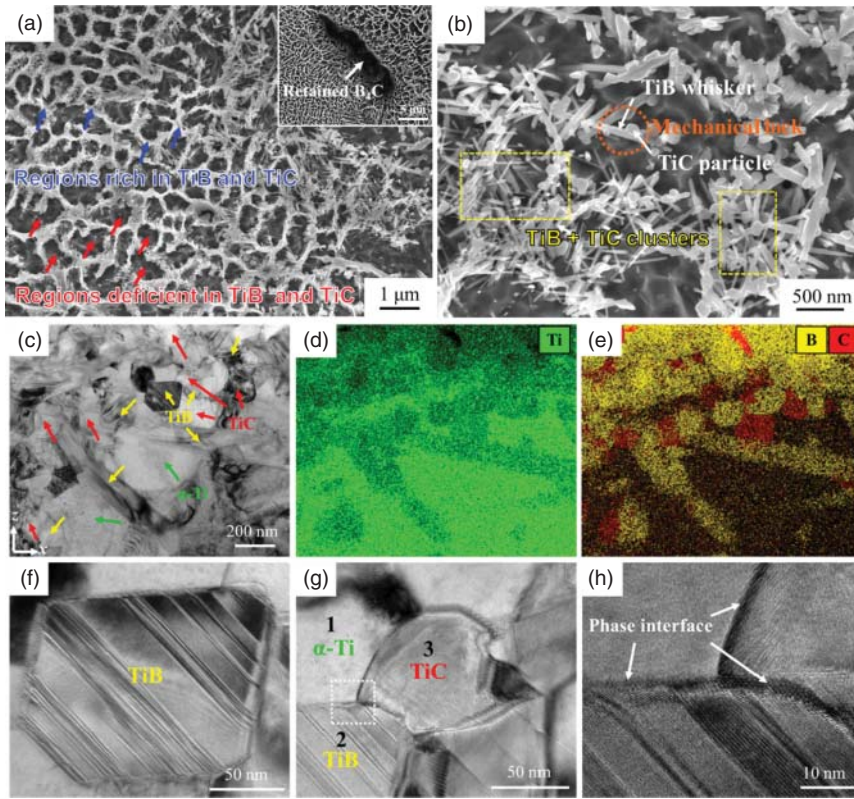


Figure 3.28 SEM images of the cellular microstructure of (TiB+TiC)/Ti composites. (a) Regions rich and deficient in the TiB whiskers and TiC particles, and the insert showing a retained B_4C particle and (b) agglomeration of TiB whiskers and TiC particles. Phase identification in the printed composites by TEM-EDS analysis: (c) TEM bright-field image; energy dispersive spectroscopy (EDS) mapping for the bright-field image showing element distributions of (d) Ti and (e) B and C; TEM images of (f) the TiB phase, (g) the coexistence of TiC, TiB, and α -Ti phases, and (h) an enlarged view of the area indicated by the white dotted rectangle in (g) displaying clear phase interfaces. Source: Han et al. (2020a)/reproduced with permission from Elsevier.

the microstructure evolved from lath α grains to acicular α' + primary cellular β grains, which led to improvements in the yield strength from 582 to 880 MPa, the tensile strength from 672 to 1186 MPa, and the microhardness from 257 to 353 HV. Moreover, the corrosion resistance of printed Ti-Ta alloys was also improved by introducing a few pits to the surface due to the rising amount of Ta_2O_5 identified through X-ray photoelectron spectroscopy (XPS).

In addition, a Ti-Ta gyroid scaffold with 25 wt% Ta was printed through LPBF. It achieved excellent elastic admissible strain (EAS), bioactivity, and *in situ* bone regeneration capability (Zhao et al. 2021), as shown in Figure 3.29. The printed scaffold with 90% porosity exhibited a good combination of low elastic modulus (1.8 GPa) and high compressive yield strength (55.5 MPa), resulting in a superb EAS (3.03%) suitable for the reconstruction of cancellous bone. The mechanisms of

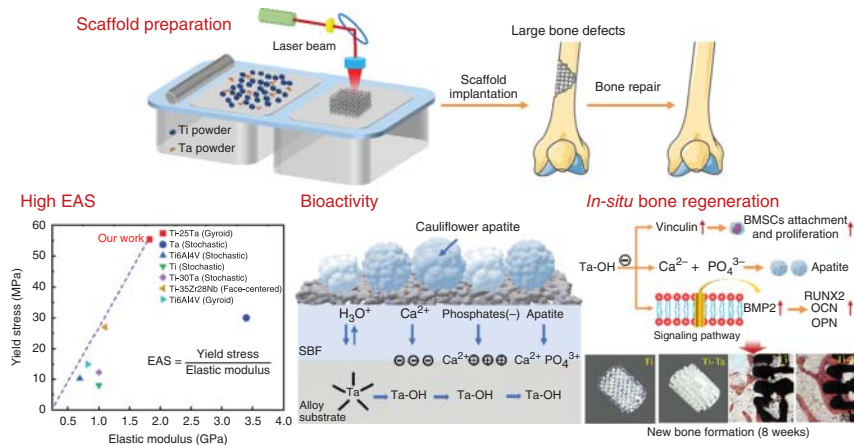


Figure 3.29 Schematic illustration of the titanium–tantalum gyroid scaffold with superb EAS, bioactivity, and *in situ* bone regeneration capability. Source: (Zhao et al. 2021)/reproduced with permission from Elsevier.

the high EAS were ascribed to the formation of $\beta(\text{Ti}, \text{Ta})$ solid solution, ultrafine β grains accompanied by nanocrystalline α' grains, and the existence of dislocations and stacking faults. In addition, bone-like apatite was spontaneously induced onto the surface of the printed Ti–Ta alloy due to the generation of a self-passivating Ta_2O_5 film, indicating a good biomineralization ability. Compared to pure Ti, the printed Ti–Ta alloy exhibited an enhanced expression of vinculin, earlier cell extension, increased nuclei density, superior cell proliferation, and the up-regulated expression of osteogenesis genes. Studies on animals further validated that the printed Ti–Ta scaffold was capable of reinforcing bone integration and accelerating bone regeneration. These findings provided a promising strategy for treating bone defects through implementing LPBF-processed metallic scaffolds.

3.7.2 Aluminum Alloys

Al alloys offer a good compromise between strength and density. Al alloys are relatively inexpensive and are therefore employed in applications where high mechanical performance and being lightweight are simultaneously required. Cast Al alloys, such as Al–Si10–Mg and AlSi12, are promising candidates for LPBF. The representative microstructures of Al–Si alloys depend on the composition and solidification condition (Dinda et al. 2013). For instance, the microstructure of LPBF-printed Al–Si10–Mg parts is typically cellular with occasional side branches; the cellular primary Al was decorated with fibrous Si particles, and Mg_2Si was precipitated out (Thijs et al. 2013).

An example of the representative microstructure of LPBF-printed Al–Si10–Mg with overlapping melt pools in the vertical and horizontal directions is shown in Figure 3.30 (Aboulkhair et al. 2016). Along the build direction, α -Al solidifies with a columnar morphology with continuous segregations of inter-dendritic Si at the

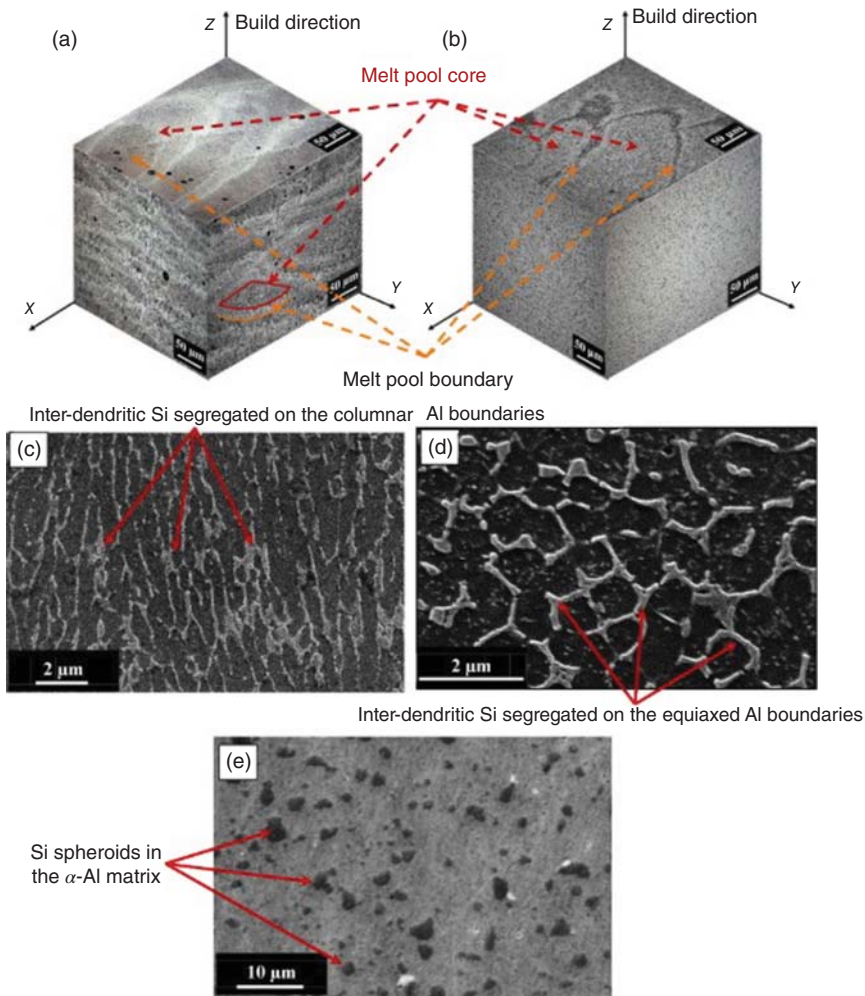


Figure 3.30 Isometric views of the microstructure of an Al-Si10-Mg alloy. (a) As-built and (b) after heat treatment, (c) elongated α -Al in the x-z plane, (d) equiaxed α -Al grains in the x-y plane, and (e) Si spheroids in the α -Al matrix after T6 heat treatment (solid solution + aging heat treatment). Source: Aboulkhair et al. (2016)/reproduced with permission from Elsevier.

boundaries (Prashanth et al. 2014). The solidification front rejected Si and deposited it into the liquid, thereby increasing its Si content during solidification. According to the Al-Si phase diagram, the solubility of Si in Al decreases as the temperature drops. High cooling rates in LPBF increased the solubility of Si in the Al matrix to ~ 7 wt% instead of the expected 1.6 wt% (Li et al. 2015a). Therefore, the formation of a cellular structure is promoted when α -Al solidifies first, leaving the residual Si to segregate at the cellular boundaries. A similar observation was made for the extended solubility of Cu and Mg in Al in AA-2024 (Zhang et al. 2016).

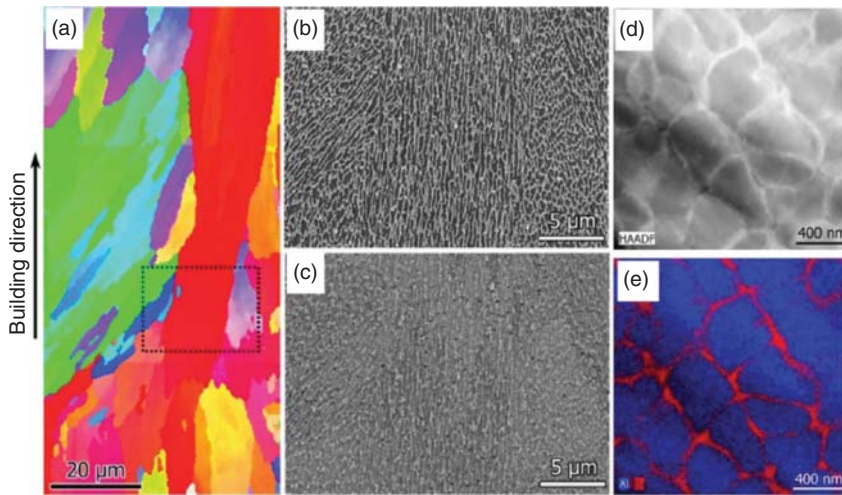


Figure 3.31 (a) Electron backscatter diffraction (EBSD) image of the grains of Al-Si10-Mg produced by LPBF with columnar cells growing parallel to the build direction. The microstructure of the dashed region in (a) obtained using (b) a secondary electron detector and (c) a backscatter electron detector. (d) A scanning transmission electron microscopy (STEM) image of the cells in the LPBF-printed Al-Si10-Mg and (e) the corresponding Al-Si EDX map. Source: Wu et al. (2016)/reproduced with permission from Elsevier.

The columnar morphology was formed as a result of the tendency of the solidifying material to perpetuate in the thermal gradient direction. The columnar cells were hundreds of microns long and 20 μm wide, as shown in Figure 3.31 (Wu et al. 2016). Scanning electron microscope (SEM) images of higher magnifications showed sub-cells in the order of 500 nm.

The inhomogeneous microstructure resulted from the liquid oscillations and temperature profile within a single melt pool. The temperature at the center of the melt pools was higher than that of other regions. Within this temperature range, an inhomogeneous microstructure with Al- and Si-rich phases was formed. The rapid cooling helped retain the Al-rich supersaturated matrix and the Si-rich nano-sized particles. The fine microstructure, alongside the abovementioned solidification mechanism, led to the formation of Al-Si10-Mg parts with a uniform dispersion of the alloying elements.

This type of microstructure validates the sequence suggested by the calculated phase diagram for Al-Si10-Mg using Calphad (Takata et al. 2018). Moreover, the microstructure was dependent on the size of the printed samples. Smaller samples in the 0.1–0.3 mm range contained Si particles inside the columnar Al grains, indicating that Si precipitation occurred during LPBF. In smaller samples, the melt pools were surrounded by regions with unmelted powder particles. Those regions exhibited lower thermal conductivity than those with a solidified material surrounding the melt pools. The lower thermal conductivity reduced the heat flow efficiency, imposing a relatively low rate of solidification, thereby prolonging the duration allowed for the precipitation of Si in the columnar Al grains at elevated temperatures.

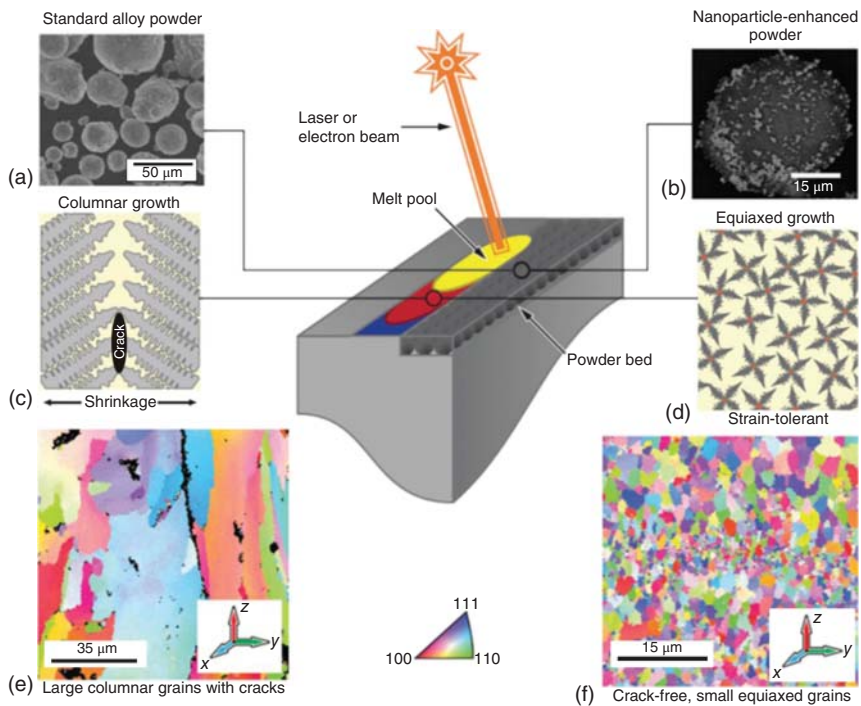


Figure 3.32 Lattice-matched nanoparticles were added to high-strength Al alloys to replace the elongated grains with equiaxed grains and avoid cracking. (a) Standard alloy powder and (b) powder after adding the nanoparticles. (c) Columnar growth and (d) equiaxed growth after the addition. (e) Columnar grains with cracks were replaced with (f) an equiaxed crack-free microstructure. Source: Martin et al. (2017)/reproduced with permission from Springer Nature.

A distinction between the microstructures was generated from the keyhole and conduction modes of melting (Qi et al. 2017). The keyhole mode contained finer grains at the melt pool boundary than the conduction mode because of the higher aspect ratio of the melt pool in the former mode.

The elongated or columnar microstructure in LPBF-printed Al alloys possesses anisotropic mechanical properties. The columnar grain growth promotes the formation of cracks during solidification (Figure 3.32). The addition of lattice-matched nanoparticles to the powder before printing can control the solidification and promote the formation of fine equiaxed grains to achieve high-strength Al alloys (Martin et al. 2017).

High thermal gradients and extreme cooling rates foster the epitaxial growth of columnar grains during LPBF processing, leading to strong crystallographic texture in most Al alloys. Such a texture results in mechanical anisotropy and crack susceptibility. The crystallographic texture in LPBF-printed Al alloys is derived from the directional solidification within the melt pools. The melt pool shape, the heat flow direction at the liquid–solid interface, and the solidification rate are crucially

affected by process parameters and the thermophysical properties of the materials (Gu et al. 2012a).

During the early stages of solidification, the average grain growth direction is the same as the solidification front direction, typically perpendicular to the melt pool boundaries (i.e. the direction of the largest thermal gradient). However, thermal gradients are predominantly formed opposite the build direction, depending on the melt pool width-to-depth ratio, as constitutional undercooling is hindered in most Al alloys due to their high thermal conductivity and propensity toward rapid solidification (Martin et al. 2017). These conditions create morphological grain texture, with the longitudinal cross-section of LPBF parts exhibiting elongated grain structures originating from the melt pool boundaries. These elongated grains are either aligned to the build direction or slanted toward the melt pool center. Such morphological grain texture is accompanied by crystallographic texture in metals and is characterized by “easy-growth” directions.

Numerous studies have validated the coupling relationship between the morphology and crystallographic textures of grains formed at the melt pool boundaries. For example, elongated grains consisting of sub-cells of identical orientation were found in an Al–Si10–Mg alloy (Wu et al. 2016). This predominant grain orientation gave rise to a $\langle 100 \rangle$ fiber texture component along the scan direction (Thijs et al. 2013), while an AlSi12 alloy also exhibited a similar texture (Suryawanshi et al. 2016). Additionally, the elongated grain structures of the Al–Si10–Mg and Al–Mg–Cu alloys were demonstrated to possess a dominant $\langle 100 \rangle$ texture along the build direction (Takata et al. 2017). Such differences were attributed to variations in the geometry of melt pools and the thermal gradients.

Equiaxed grains possess no predominant crystallographic texture, which is advantageous for minimizing mechanical anisotropy. The addition of suitable heterogeneous elements increases the density of nucleation sites in melt pools and facilitates the columnar-to-equiaxed transition of the grain structure. This approach is effective in promoting refined texture-free melt pool grain structures in several Al alloys, including Al–Mg–Zr, AA-2xxx series, Al6061, and Al7075.

Additionally, the intensity of crystallographic textures depends on the combination of different individual melt pools and tracks. During the partial remelting of the neighboring tracks, any refined equiaxed structures formed in the latter stage of solidification can be reduced at the expense of elongated textured grains. The hatch spacing, layer thickness, and scanning strategy selected may influence texture intensity (Thijs et al. 2013; Qi et al. 2017). Inter- and intra-layer rotation scanning strategies have been proven effective in weakening the texture. Melt pools formed by the moving laser source are elongated in shape, and rotating the scan direction reduces the amount of remelted material compared to uni/bi-directional scanning strategies. This strategy can promote the retention of the randomly orientated equiaxed grain structures formed in solidified melt pools (Figure 3.33).

To address the challenges of crack suppression and microstructure control in wrought aluminum alloys, a novel Ti-modified Al–2.25Cu–1.8Mg alloy was developed through thermodynamic calculations of the cracking susceptibility factor,

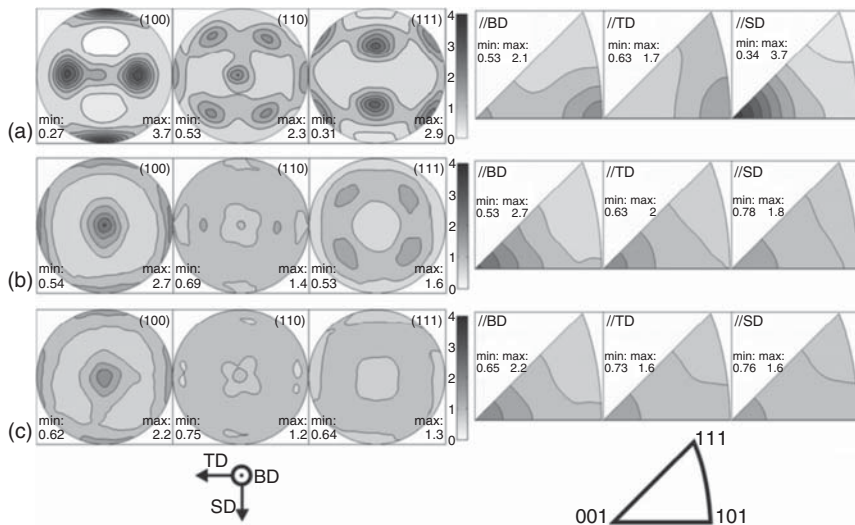


Figure 3.33 Contour pole figures and inverse pole figures of LPBF-printed Al-Si10-Mg samples were produced using (a) unidirectional, (b) bidirectional, and (c) chessboard scan strategies. Source: Reproduced from Thijs et al. (2013)/with permission from Elsevier.

growth-restriction factor, and phase diagram based on the Scheil solidification model, as shown in Figure 3.34a–c (Zhang et al. 2021). Before modification, the Al-Cu-Mg alloy exhibited a textured coarse microstructure with hot tearing cracks distributed along its columnar grains (Figure 3.34d). The addition of 1.5 wt% Ti effectively promoted the columnar-to-equiaxed grain transition and grain refinement due to the formation of Al_3Ti nanoparticles (Figure 3.34e). The LPBF-processed Ti-modified Al-Cu-Mg alloy was crack-free and possessed superior mechanical properties, such as a high ultimate tensile strength of 426.4 MPa, a yield strength of 293.2 MPa, and an elongation to failure of 9.1%. In contrast, the ultimate tensile strength of the LPBF-fabricated Al-Cu-Mg alloy without Ti modification is only 173.2 MPa, with an elongation to failure of less than 2% due to the high level of hot cracking (Figure 3.34f).

3.7.3 Nickel Alloys

Nickel-based alloys possess excellent corrosion resistance and mechanical properties at elevated and low temperatures, making them critical superalloys for industrial applications. Additionally, these alloys exhibit outstanding wear resistance, magnetic properties, and high electrical resistance.

Among the refractory nickel-based alloys, Inconel alloys are resistant to corrosion by chlorine, fluorine, and solutions containing ions of these elements at elevated temperatures. In addition, Inconel alloys have displayed better resistance to progressive oxidation at 1100 °C and in an oxidizing-sulfide atmosphere at 850 °C as they are not vulnerable to vapor, ammonia, or sulfur-containing gas. Due to these properties,

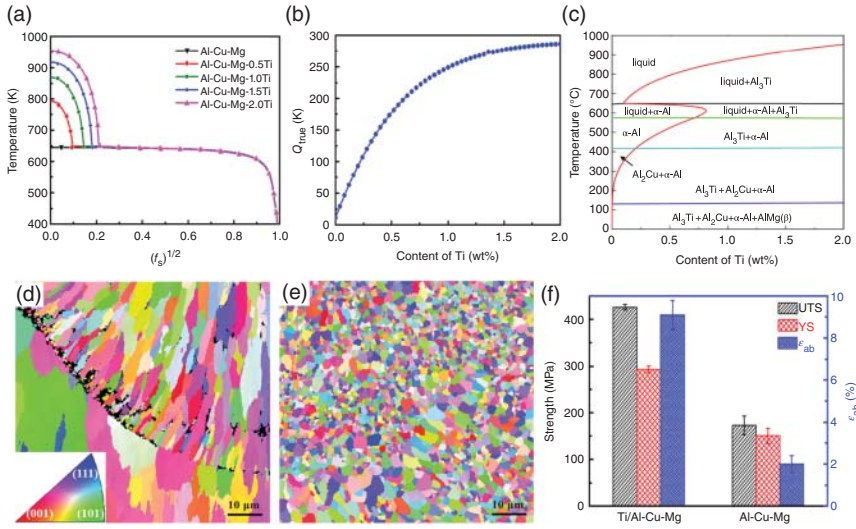


Figure 3.34 (a) Relationship between temperature and the fraction solid f_s , (b) variation in the growth restriction factor Q_{true} with Ti content, and (c) the phase diagram of Al-Cu-Mg-xTi alloys; IPF maps of (d) Al-Cu-Mg and (e) Ti/Al-Cu-Mg samples, and (f) their mechanical properties. Source: Zhang et al. (2021)/reproduced with permission from Elsevier.

Inconel alloys are selected to manufacture steam and gas turbines and parts for the aerospace and nuclear industries.

The formation of precipitates and intermetallic compounds in nickel-based alloys is critical to their mechanical properties. The austenite γ and Laves phases are dominant in the LPBF-built Inconel 718, with almost no other phases, while subsequent heat treatment can promote the precipitation of the γ' and γ'' phases (Amato et al. 2012; Li et al. 2018b). Figure 3.35a presents a magnified 3D transmission electron microscope (TEM) image of the alloy, which exhibits a variety of dense precipitates within the columnar $[100]$ arrays composed of apparent array boundaries. The horizontal surface contains oblate ellipsoidal or spheroidal particles as large as 250 nm immersed in a dense field of precipitates <10 nm in diameter inside or at the boundaries of equiaxed arrays. Well-defined columnar arrays of elongated precipitates coincident with (100) are observed in the vertical reference plane parallel to the build direction.

Figure 3.35b provides a schematic composite displaying these features as they relate to the scan geometry and melt pool-related layer development, as well as the columnar arrays formed by the directional, epitaxial-like solidification pertaining to the high temperature gradients during the LPBF process. The stacks of disc-like or oblate spheroidal γ'' precipitates appear to be created in successively formed melt pools due to their short interaction time and highly conductive heat transfer, which is possibly facilitated by the argon or nitrogen gas environments or their corresponding thermal conductivities.

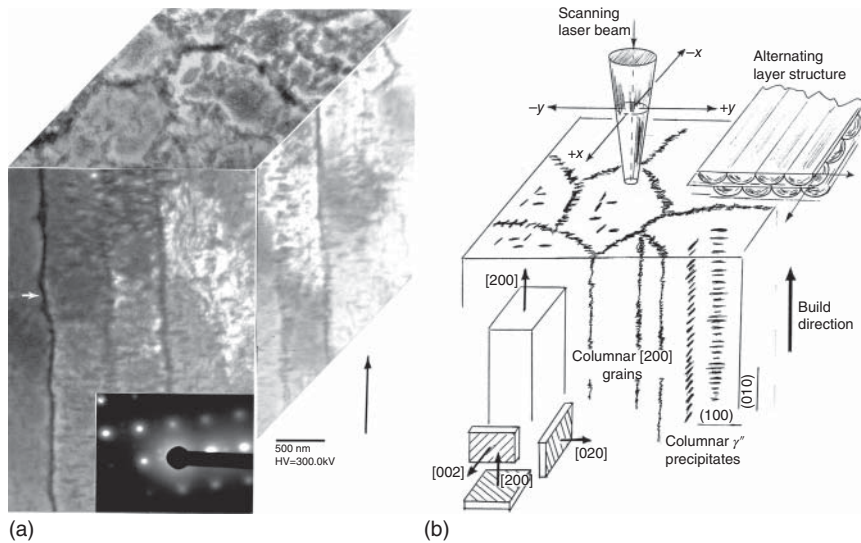


Figure 3.35 (a) 3D TEM image composite view for an as-fabricated cylinder along the z axis with HIP treatment. Inset: selected area electron diffraction (SAED) pattern corresponding to a γ $[0\ 0\ 1]$ zone in the vertical reference plane. (b) A schematic illustrating the directional solidification-induced columnar γ'' precipitates and the melt pool development in LPBF. Source: Amato et al. (2012)/reproduced with permission from Elsevier.

Comparatively, Inconel 625, a solid solution-strengthened superalloy, is primarily strengthened by Mo and Nb elements. The as-built microstructure of an LPBF-printed Inconel 625 superalloy was austenite with high solution distortions but no carbide precipitation (Li et al. 2015b). After heat treatment, a large number of NbC and MoC carbide precipitates were produced from the matrix. When the samples were treated at 700 °C, the Nb element precipitated and the γ'' (Ni_3Nb) phase was formed. Therefore, the lattice constants decreased accordingly. When the temperature rose to 850 °C, the γ'' phase transformed into a new stable structure of orthorhombic δ (Ni_3Nb). The inverse pole figure (IPF) of the y - z and x - y planes showed that the individual grains with different crystal orientations were represented by different colors (Figure 3.36). Some of the larger elongated grains were several hundred micrometers long and grew across a few layers. A strong texture could be identified for the LPBF-printed sample.

The nucleation of γ' - $\text{Ni}_3(\text{Al}, \text{Ti})$ phase precipitates and the unexpected δ - Ni_3Nb precipitates were observed because of the significant microsegregation of niobium caused by the rapid heating and cooling cycles (Idell et al. 2016). The nucleation of δ precipitates was restricted when the local content of niobium was less than 6.8% molar fraction. By increasing the laser energy, the coarsening effect led to a larger size of the γ' precipitates. As the sample was built up, the previous layer experienced an aging treatment, which further promoted the formation of the γ' phase.

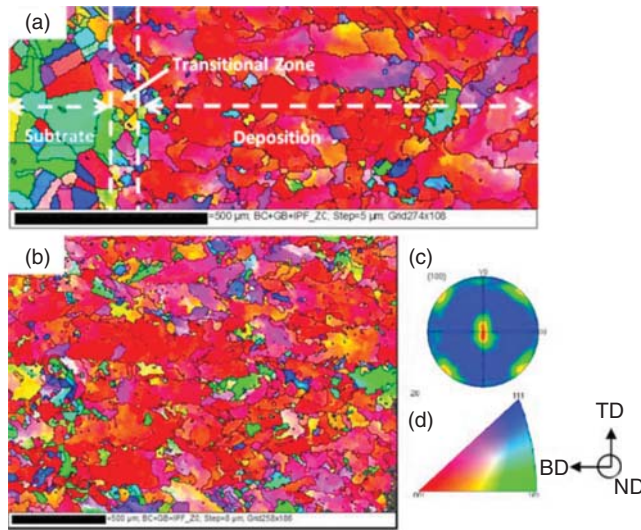


Figure 3.36 Microstructure morphology of an LPBF-printed Inconel 625 superalloy. Inverse pole figure (IPF) colored map of (a) the y - z plane and (b) the x - y plane. (c) (100) pole figure, and (d) the index map of the IPF, including the reference coordinates. Source: Li et al. (2015b)/reproduced with permission from Elsevier.

3.7.4 Iron Alloys

Iron-based alloys are the most common engineering materials in industries. Steels available for LPBF are predominantly common austenitic stainless steels (316L and 304L), maraging steel (18Ni-300), precipitation-hardening stainless steels (17-4 PH, AISI: 630 and 15-5 PH), martensitic cutlery steels (AISI 420), tool steels (H13), etc. Besides steels, iron-based alloys and intermetallics, such as Fe-Ni, Fe-Ni-Cu-P, Fe-Ni-Cr, Fe-Al, and Fe-Cr-Al alloys, have also been processed through LPBF.

Most research publications on the LPBF processing of iron-based alloys are based on 316L stainless steel. Abe et al. conducted preliminary tests on this material in 2001, but they were unsuccessful due to balling effects (Abe et al. 2001). The first paper that reported the successful printing of 316L stainless steel through LPBF was published in 2005 (Jandin et al. 2005). In this study, a ytterbium fiber laser with a wavelength of 1065 nm was used to process the 316L stainless steel powder. The experiment indicated that low laser power and high scanning speed led to incomplete melting of the powder material and resulted in components with high porosity. However, 316L stainless steel could achieve 99.9% relative density with LPBF (Tolosa et al. 2010).

Figure 3.37 displays a typical hierarchical microstructure obtained in LPBF-printed 316L (Wang et al. 2018). The 316L alloy was highly heterogeneous, comprising millimeter-sized grains to nanometer-sized precipitations. Compared to conventional pure metals and alloys fabricated by casting, LPBF-printed parts display a gradient transition of crystal orientations within each grain (the grain boundary is defined by a misorientation $>10^\circ$), as shown in Figure 3.37b. Because

of the high thermal gradient and rapid cooling, there was insufficient time for the atomic lattices to be regularly packed, leading to the orientation transition gradient. Moreover, the low- and high-angle grain boundaries were highly dense and irregular (Figure 3.37g,h). Unlike alloys manufactured through casting or molding, the fabricated parts exhibit a cellular microstructure because of the unique temperature gradient and cooling rate conditions in LPBF. Under scanning transmission electron microscopy (STEM), segregations of Mo and Cr were detected near the cellular boundaries. Moreover, nano-inclusions precipitated preferentially along the cellular walls, which induced dislocation pinning and promoted the formation of deformation twinning. The elemental segregation near the cell walls of the cellular structure was highly dependent on the processing conditions.

In addition to 316L, other austenitic stainless steels typically possess a completely austenitic microstructure after LPBF. For example, 304L alloys exhibited elongated grains in the build direction with a 100% austenitic phase and no precipitation of chromium carbides at grain boundaries (Abd-Elghany and Bourell 2012). However, the microstructure of 17-4 PH consisted of 72% austenite and 28% martensite with highly twinned martensite plates and untwinned regions near the martensitic grains with a high density of stacking faults and dislocations (Facchini et al. 2010). The retained austenite was located between the martensite plates, which mainly resulted from residual thermal stresses in the material formed under rapid cooling during LPBF, stabilizing the metastable austenitic phase (LeBrun et al. 2015).

In AISI 420, an austenitic phase may exist due to austenite reversion (Krakhmalev et al. 2015). The top layers revealed a mixed microstructure of fresh martensite and 21% of retained austenite. In contrast, the center of the specimens appeared to be composed of tempered martensite with ~57% austenite. Austenite reversion was also reported to occur during aging precipitation hardening of 17-4 PH, during which the diffusion of Ni and Cu in conjunction with the formation of precipitates led to a similar effect (LeBrun et al. 2015). However, with heat treatment (>550 °C for four hours), the austenite generated in LPBF was observed to partially transform to martensite since the relief of residual stresses might enable the austenite to martensite transformation during post-treatment cooling. The LPBF-printed maraging steel (18Ni-300) also exhibited austenite reversion with Ni-rich reverted austenite shells around the retained austenite regions during aging, as shown in Figure 3.38 (Jägle et al. 2014).

Austenitic stainless steels include γ -austenite and δ -ferrite when processed by LPBF but are generally fully austenitic when manufactured conventionally. In austenitic stainless steels printed by LPBF, no clear trend can be identified regarding yield strength and ultimate tensile strength as linear or volumetric heat input functions. 17-4 PH and 15-5 PH are two widely studied precipitation-hardening stainless steel materials for the LPBF printing process. When processed in a nitrogen atmosphere, the as-printed parts consist of a mixture of austenite (50–75 vol%) and martensite (25–50 vol%), in contrast to the mostly martensite phase (92 vol%) formed in the parts when processed in an argon atmosphere (Rafi et al. 2014; Murr et al. 2012). Heat treatment results in the desired precipitation of Cu-rich particles within a martensitic matrix. The LPBF-printed parts generally exhibit lower yield

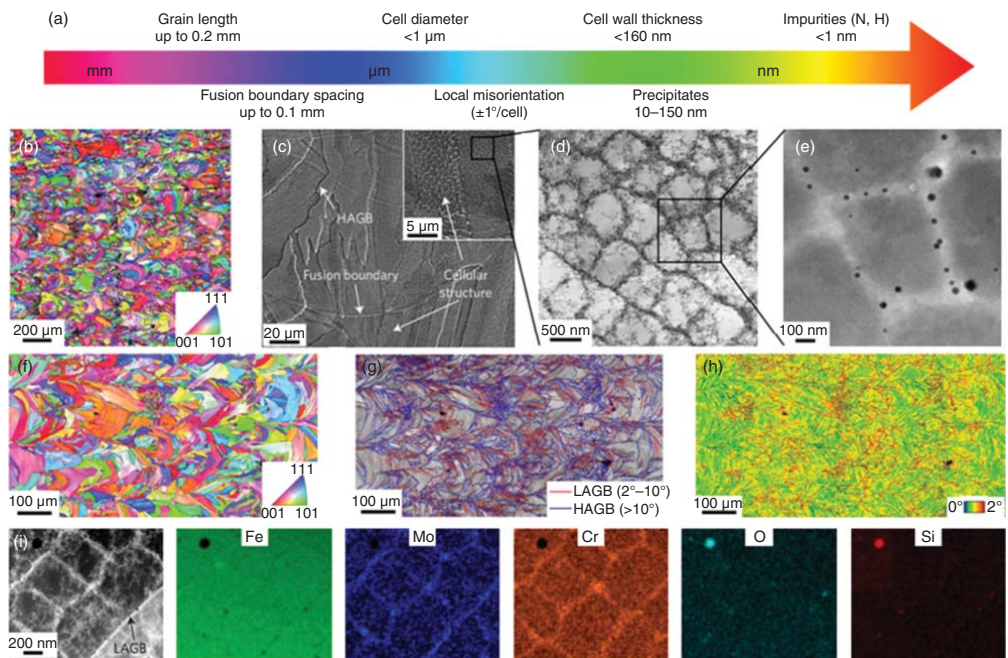


Figure 3.37 A typical microstructure of an LPBF-printed 316L stainless steel. (a) Schematic of microstructures at various length scales, (b) cross-sectional EBSD IPF map of the printed sample showing the grain orientations, (c) cross-sectional SEM image revealing fusion boundaries, high-angle grain boundaries, and solidification cellular structures, (d) TEM image of solidification cells, (e) high-angle annular dark-field (HAADF) image of the solidification cells shown in (d), (f) EBSD IPF map at a higher magnification, (g) EBSD image quality map with grain boundaries, (h) map of the kernel average misorientation, and (i) HAADF image presenting the segregation of Mo and Cr from the solidified cellular walls and low-angle grain boundaries. Source: Wang et al. (2018)/reproduced with permission from Springer Nature.

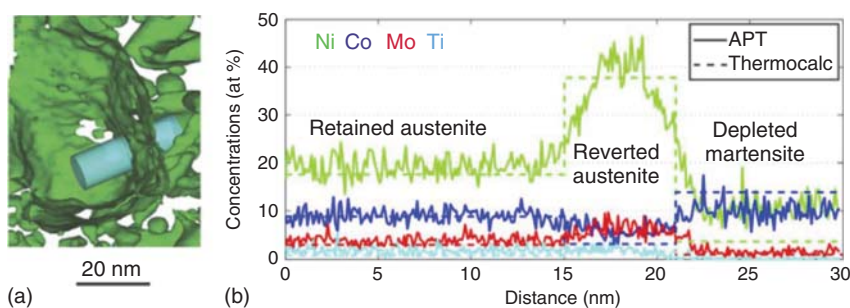


Figure 3.38 Re-austenitization of LPBF-printed maraging steel during aging at 480 °C/5 h. (a) Location of atom probe tomography (APT) and (b) concentration profile along the cylinder shown in (a) for the Ni, Co, Mo, and Ti elements. Source: Jäggle et al. (2014)/reproduced with permission from Cambridge University Press.

strength and hardness than their heat-treated wrought counterparts, which is most likely due to the relatively soft retained austenite in the printed parts. A strain-induced phase transformation from austenite to martensite occurs during the plastic deformation of the LPBF-printed parts, resulting in a high strain hardening.

3.7.5 Others

3.7.5.1 Cobalt Alloys

Co-based materials can withstand extreme service conditions such as high temperatures and corrosive environments. Their applicability in orthopedic implants has also been demonstrated. These materials are among the hardest biocompatible alloys with high wear and corrosion resistance, and they are employed in biomedical applications, such as dental, joint, and fracture fixation. Co–Cr–Mo and Ni-free Co–Cr–W alloys produced by LPBF are commonly investigated. Co–Cr–Mo alloys have been widely utilized to manufacture removable partial dentures, metal frames, and porcelain-fused-to-metal crowns in dentistry. For Co–29Cr–6Mo alloys, dense builds were obtained when the input energy of the laser scan was higher than 400 J/mm³ (Takaichi et al. 2013). A unique microstructure was obtained with fine cellular dendrites in the elongated grains parallel to the build direction. The γ phase was dominant in the build, and a preferential $\langle 001 \rangle$ orientation was observed along the build direction at low energy input. For Co–Cr–W alloys, the microstructure consisted of γ and ϵ phase in a square-like pattern with fine cellular dendrites at the borders (Lu et al. 2015).

3.7.5.2 Copper Alloys

Copper and its alloys exhibit high electrical and thermal conductivity and are some of the most essential conducting materials utilized in electrical components, heat sinks, and tooling inserts. Cu–Cr and Cu–Cr–Zr alloys are widely used in aerospace and nuclear industries; however, binary Cu–Cr alloys are known to suffer from dynamic embrittlement due to the segregation of sulfur elements at grain boundaries. Minor additions of Zr and Ti can improve the hot ductility of

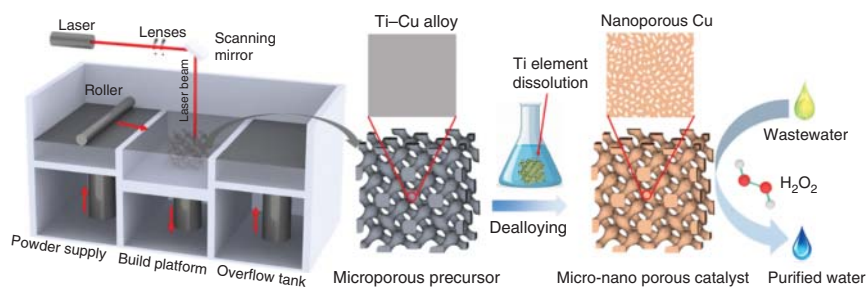


Figure 3.39 Schematic of the preparation procedure of a micro- and nanoporous Cu catalyst via LPBF and dealloying and its application as a heterogeneous Fenton-like reagent for wastewater remediation. Source: Reproduced from Cai et al. (2021a)/with permission from American Chemical Society.

Cu-Cr alloys by forming zirconium and titanium sulfides. The microstructure of LPBF-printed Cu-Cr-Zr-Ti alloys consisted of grains elongated along the build direction with sizes ranging from 30 to 250 μm (Popovich et al. 2016).

A representative study combined LPBF with chemical dealloying to develop a hierarchical micro- and nanoporous catalyst for functional applications (Cai et al. 2021a). A diamond cellular structure with micropores, which was a typical triply periodic minimal surface (TPMS) cellular structure, was printed as alloying precursors via LPBF from mechanically mixed Ti and Cu powders. Subsequently, chemical dealloying was utilized to leech Ti from the printed Ti-Cu structure precursors to create a nanoporous Cu-encapsulating catalyst. Finally, the catalyst was utilized as a heterogeneous photo-Fenton-like reagent to degrade dye pollutants in wastewater (Figure 3.39).

The dealloyed catalyst still retained the microscale porous framework of the as-printed structure precursors, while its surface color changed from silver to a shade of copper after dealloying (Figure 3.40a). The color variation stemmed from the corrosion dissolution of Ti and the self-assembly diffusion of Cu on the surface of the structure precursors upon dealloying. The dealloyed catalyst was covered with 3D open-nanopore structures several micrometers thick, which comprised continuous ligaments and pores with sizes in the range of 10–90 nm (Figure 3.40b,c). The hierarchically interconnected micro- and nanoporous structures contributed to the catalyst having a remarkable degradation efficiency and attractive stability. This work manifests the applicability of the developed catalyst to wastewater purification in practical applications. Furthermore, it inspires incorporating AM and chemical synthesis to design high-performance metal catalysts with tunable hierarchical micro- and nanopores for functional applications.

3.7.5.3 Magnesium Alloys

Magnesium-based materials are primarily employed to develop lightweight structures because of their low density. Hence, they are in high demand in the automotive, aerospace, and biomedical industries. Notably, the complete melting of a single magnesium track using a miniature LPBF system in an inert argon gas atmosphere was

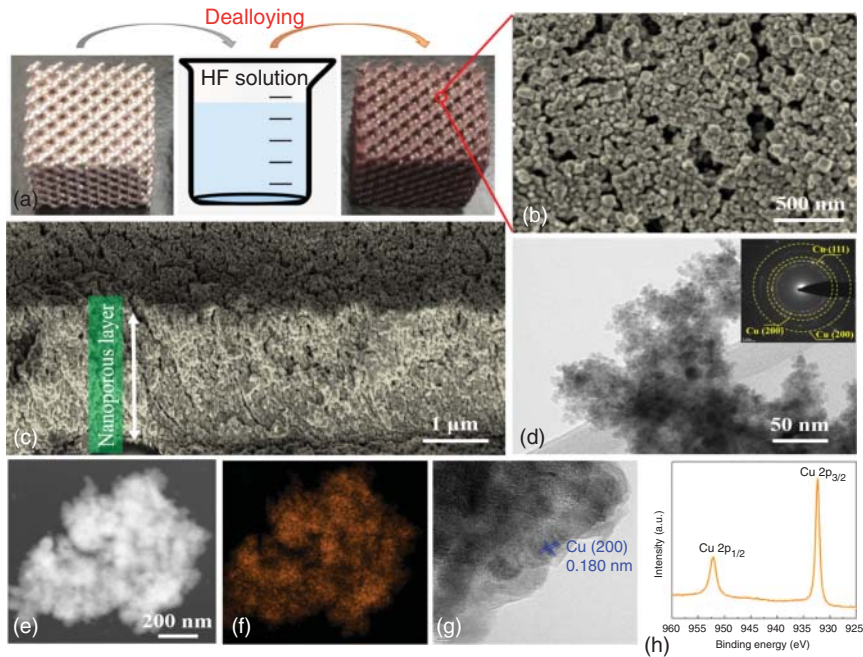


Figure 3.40 Characterization of the catalyst. (a) Photographs of the structure before and after dealloying, (b) plan-view morphology and (c) cross-sectional morphology of the nanoporous copper layer, (d) TEM image of the nanoporous copper layer and corresponding selected area electron diffraction; EDS mapping profile of (e) the original image and (f) Cu element distribution; (g) high-resolution TEM image of the boundary of a cluster of the nanoporous copper layer, and (h) XPS spectra of the Cu 2p orbitals of the nanoporous copper layer. Source: Reproduced from Cai et al. (2021a)/with permission from American Chemical Society.

achieved (Ng et al. 2010). Additionally, the interactions between the laser source and Mg powder tracks under different laser powers, scanning speeds, and irradiation modes (i.e. continuous wave and pulsed mode) have been investigated (Ng et al. 2011). Additionally, several investigations have focused on developing processing windows for Mg and its alloys, such as Mg–9%Al, AZ91D, ZK60, and WE43 (Savalani and Pizarro 2016; Zhang et al. 2012; Wei et al. 2014). The microstructures of Mg alloys consist of equiaxed α -Mg grains with sizes of 1–20 μm , which are often accompanied by the formation of partially or fully divorced eutectic phases (the separation of eutectic phases) homogeneously distributed along the grain boundaries.

The difficulties faced in the LPBF processing of Mg alloys mainly consist of two aspects. On the one hand, ductile oxide layers form rapidly due to the high affinity of Mg for oxygen during LPBF. As a result, the Mg oxide film can reduce the bonding strength between the powders, which results in various metallurgical defects. On the other hand, Mg exhibits a narrow temperature range (440 °C) between its boiling point and melting point and is thus easily evaporated under a high-power laser input. Such vaporization can increase the surface roughness and defects

(such as pores and cracks) of printed parts. Moreover, Mg alloy powders are highly flammable, and extra caution must be taken when processing them through LPBF.

3.7.5.4 High-Entropy Alloys

HEAs are emerging as a novel frontier in the metal materials community and, hence, have gained extensive research interests in academia and industry. LPBF has been introduced to print HEA parts because of its capability to produce complex components with outstanding mechanical properties (Han et al. 2020b). Efforts have been expended on the LPBF printing of HEAs, such as AlCoCrFeNi, AlCoCuFeNi, AlCrCuFeNi, CoCrFeNi, CoCrFeMnNi, CoCrFeNiC, CoCrFeNiTiMo, MoNbTaW, and NiCrWFeTi. Combinations of different element types and proportions can form different solid solution phases. The high cooling rates in LPBF lead to unique and refined microstructures for the printed HEA parts. For example, the laser energy density influences the microstructural evolution of LPBF-printed CoCrFeMnNi and AlCoCrFeNi HEA parts (Li et al. 2018a; Niu et al. 2019). An increase in the energy density from 37 to 185 J/mm³ did not change the face-centered cubic (FCC) phase of CoCrFeMnNi but decreased its lattice parameter through the vaporization of Mn. The high cooling rates in LPBF led to large degrees of undercooling in melt pools, thus resulting in sub-micro cellular grains in the CoCrFeMnNi HEA parts. Presently studied HEAs exhibit a wide range of mechanical properties with a yield strength of 402–773 MPa, an ultimate tensile strength of 480–1178 MPa, an elongation of 8–34%, and a microhardness of 212–829 HV.

3.8 Mechanical Metamaterials for LPBF

Metamaterials are introduced in this section, as most of them are fabricated by LPBF. In contrast, only a few are fabricated by electron beam melting to study metamaterials by metal AM.

Porous structures, also called cellular structures, are developed through the biomimicry of natural cellular materials, including wood, cork, and human bone, for their high strength-to-weight ratios (Banhart and Seeliger 2008). Due to its high printing resolution, LPBF has been extensively used to fabricate porous structures with customized shapes and controllable pore geometries. Porous structures can be classified into two categories, i.e. foam and lattice structures. Foam structures can be prepared by injecting gas or mixing a foaming agent into a molten metal or polymer at a low cost. However, irregular pores are often obtained during the preparation of foam structures, often resulting in an inconsistent mechanical response that must be rectified via conservative designs (i.e. with a high safety factor). Lattice structures refer to two-dimensional (2D) or 3D geometries constructed by rationally arraying unit cells. A unit cell is the minimal architecture required to construct a lattice structure. In early studies, lattice structures were often referred to as cellular solids or structures due to the formation of interconnected networks by solid struts or plates (Gibson and Ashby 1997). These artificial lattice structures are subsequently included in the field of metamaterials.

3.8.1 Fundamentals of Mechanical Metamaterials

The initial concept of metamaterials originated from a work that employed an artificially twisted structure to polarize an electromagnetic wave (Bose 1898). Metamaterials possess extraordinary physical properties, such as electromagnetic/acoustic cloaking, a zero/negative Poisson's ratio, and a negative refractive index. Therefore, metamaterials have been progressively applied in optics, acoustics, mechanics, etc. They can be categorized into mechanical metamaterials, electromagnetic metamaterials, acoustic metamaterials, and thermal metamaterials (Figure 3.41) (Fan et al. 2021).

Mechanical metamaterials exhibit unusual mechanical properties, which are determined by their geometries instead of their material composition. Therefore, they are the most extensively fabricated structures by LPBF among all the metamaterial categories. They can be further classified into three categories based on their fundamental elastic constants, i.e. Young's modulus, shear/bulk modulus, and Poisson's ratio (Yu et al. 2018), as shown in Figure 3.42.

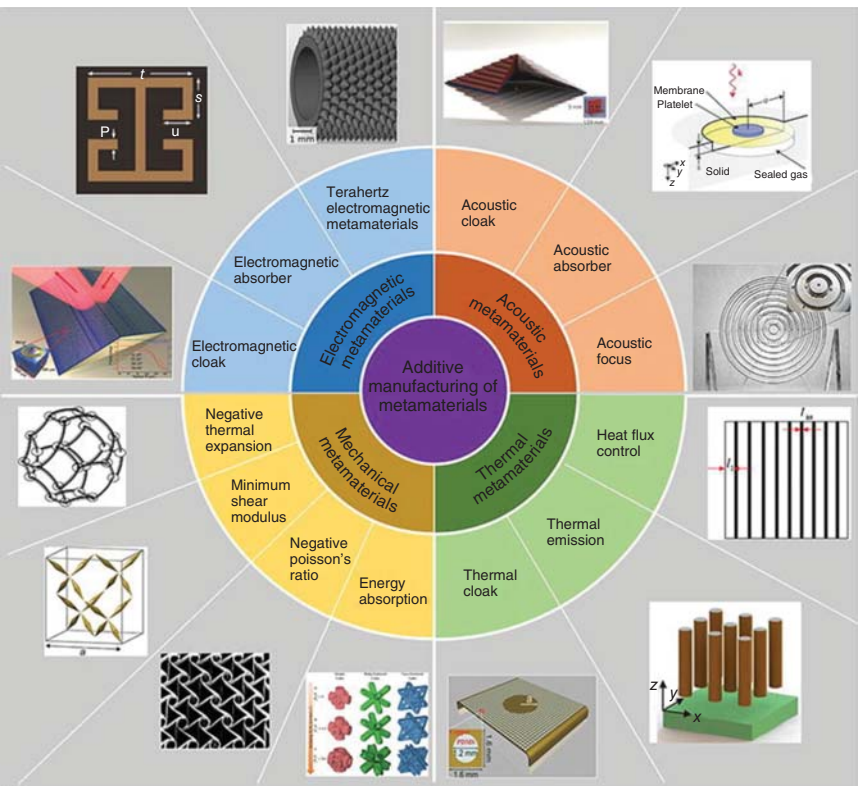


Figure 3.41 Classification of metamaterials according to their functionalities. Source: Fan et al. (2021)/reproduced with permission from Elsevier.

3.8.2 Mechanical Metamaterials with High Young's Modulus

Mechanical metamaterials with a high Young's modulus include high-strength-to-weight lattices and their derivatives, such as origami-inspired metamaterials and cellular origami structures.

High-strength-to-weight lattices consist of strut-based (open-cell) and shell-based (usually in closed-cell) structures. They are the earliest known mechanical metamaterials inspired by the crystalline structures of metals.

Origami-inspired structures include three main types of designs: the Miura-ori pattern, the nonperiodic Ron Resch pattern, and the square twist pattern. In addition, the Kirigami pattern is considered a special type of origami metamaterial design.

Cellular origami metamaterials result from the 3D manipulation of the Miura-ori pattern. The study on the behavior of pattern transformation metamaterials focuses

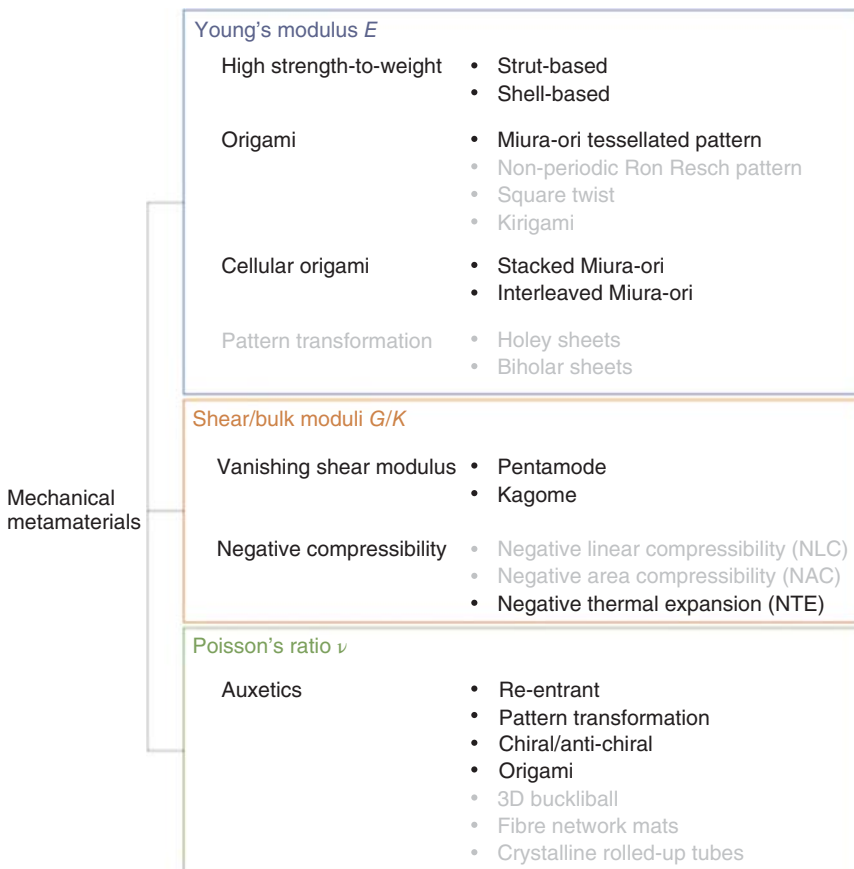


Figure 3.42 Classification of mechanical metamaterials. LPBF-printed mechanical metamaterials are in black.

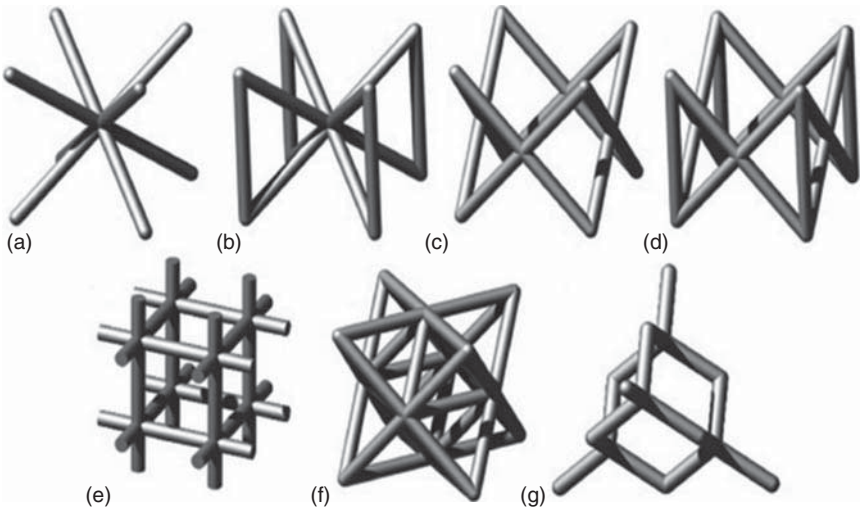


Figure 3.43 Strut-based lattice structures. (a) BCC, (b) BCCZ, (c) FCC, (d) FCCZ, (e) cubic, (f) octet-truss, and (g) diamond. Source: Reproduced from Maconachie et al. (2019)/with permission from Elsevier.

on the tunability of the stiffness. Pattern transformation metamaterials, such as holey and bipolar sheets, can induce changes in material properties based on the threshold deformation in their mechanical designs.

The fundamental strut-based lattice structures consist of BCC and FCC unit cell topologies, including their variations (Figure 3.43a–d) (Maconachie et al. 2019). These unit cells are named after analogous crystalline structures, while other types of strut-based topologies include cubic, octet-truss, and diamond structures (Figure 3.43e–g). The simplicity of these strut-based designs has attracted much attention previously. Recent studies of strut-based topologies have sought to maximize the efficiency of material distribution within the unit cell space through topological optimization, which can only be materialized through AM.

The Maxwell number M is widely adopted to characterize the strut-based topologies in terms of their mechanical properties (Deshpande et al. 2001). It is given by

$$M = s - 2n + 3, \quad (3.7)$$

$$M = s - 3n + 6, \quad (3.8)$$

where s is the number of struts, and n is the number of nodes. Equations (3.7) and (3.8) are applied for truss topologies in 2D and 3D spaces, respectively. If M is negative, the number of struts to equilibrate external forces is insufficient, resulting in bending stress due to moments developed in the struts, which leads to bending-dominated behavior. Meanwhile, suppose M is greater than or equal to zero. In that case, external loads are equilibrated by axial tension and compression in the struts, indicating that no bending occurs at the nodes and rendering such structures stretch-dominated (Leary et al. 2018). Due to these phenomena, stretch-dominated

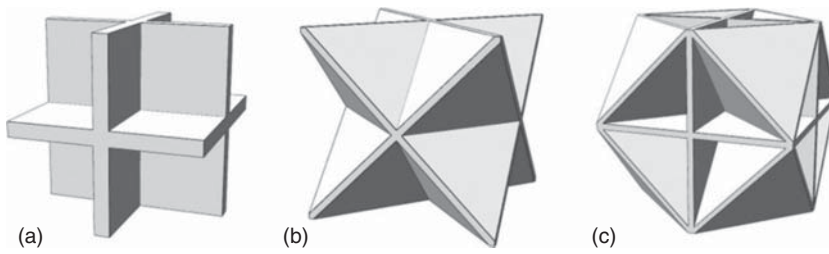


Figure 3.44 Representative topologies of the unit cells for shell lattice structures. (a) Cubic, (b) octet, and (c) Cubic + octet structures. Source: Reproduced from Berger et al. (2017)/with permission from Springer Nature.

structures are stiff and strong but lightweight, while bending-dominated structures are compliant.

LPBF has been employed to fabricate strut-based lattice structures, such as BCC, FCC, and cubic structures. The effect of cell topologies (BCC, FCC, and cubic structures) on the compressive properties of LPBF-printed structures for bone implant applications was investigated through numerical and experimental methods (Han et al. 2017b). The numerical results indicated that different unit cell topologies resulted in distinct stress distributions on the bearing struts of scaffolds, while the unit cell size directly determined the stress value. The LPBF-printed BCC structure was coated with silk fibroin/gentamicin through the electrophoretic technique to prevent postoperative infections of LPBF-printed bone substitutes (Han et al. 2017c). With the development of design optimization tools, the structural and mechanical properties of a topologically optimized Ti-6Al-4V cellular interbody fusion cage were investigated to maintain spine segmental integrity (Lin et al. 2007).

The lightweight design enables a decrease in density and an increase in the mechanical strength of LPBF-printed strut-based structures. The low-velocity impact responses of LPBF-printed Ti-6Al-4V and 316L sandwich structures have been investigated through localized drop weight testing (Mines et al. 2013). The impact resistance of Ti-6Al-4V BCC lattice was comparable to that of the conventionally manufactured honeycomb sandwich panels. However, the printing quality, such as the surface finish, of the 316L BCC sandwich structure was superior to that of the Ti-6Al-4V structure, although the former exhibits a lower specific strength.

Shell lattice structures are another type of cellular structure with unit cells composed of plates instead of struts (Berger et al. 2017). This type of lattice structure is fundamentally a closed-cell lattice formed by thin walls. Representative unit cells for shell lattice structures are shown in Figure 3.44, including cubic, octet, and cubic + octet structures. For the same density, shell lattice structures have demonstrated superior elastic properties relative to strut-based structures (Tancogne-Dejean et al. 2018). Nevertheless, unlike open-cell strut-based structures, LPBF processing of closed-cell shell lattice structures encounters difficulty with powder removal.

Recently, TPMS-based structures have gained much popularity and have been extensively fabricated through LPBF. They are characterized by locally minimized

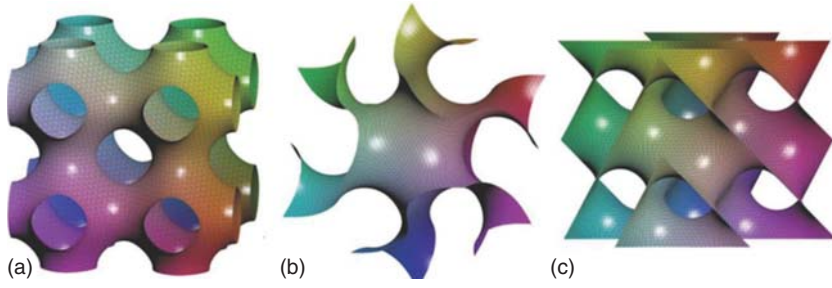


Figure 3.45 Schematic drawings and skeletal graphs of TPMSs. (a) Primitive, (b) gyroid, and (c) diamond surfaces. Source: Reproduced from Han and Che (2018)/with permission from John Wiley & sons.

surface area for a given boundary such that the mean curvature at each point on the surface is zero. Fundamental types of TPMS are primitive, gyroid, and diamond surfaces (Figure 3.45) (Han and Che 2018). A primitive TPMS possesses two intertwined congruent labyrinths, each with the shape of an inflated tubular version of the simple cubic lattice. A gyroid TPMS separates the space into two oppositely congruent labyrinths of passages that run through the surface in a gyrating pattern. It is the only known embedded TPMS with triple junctions and no lines of reflectional symmetry. Finally, a diamond TPMS has two intertwined congruent labyrinths, each with the shape of an inflated tubular version of the diamond bond structure.

The surface of the three aforementioned TPMS models possesses a mean curvature of zero, which can be extended indefinitely in the three periodic directions to provide a concise description of many physical structures. A parametric TPMS is characterized by the Weierstrass formula to generate its coordinates, which is defined as

$$\begin{cases} x = \text{Re} \int_{\omega_0}^{\omega_1} e^{i\theta} (1 - \omega^2) R(\omega) d\omega \\ y = \text{Re} \int_{\omega_0}^{\omega_1} e^{i\theta} (1 + \omega^2) R(\omega) d\omega, \\ z = \text{Re} \int_{\omega_0}^{\omega_1} e^{i\theta} (2\omega) R(\omega) d\omega \end{cases} \quad (3.9)$$

where θ is an angle known as the Bonnet, ω represents a complex variable, and $R(\omega)$ represents a function that varies with different surfaces. For primitive, gyroid, and diamond surfaces, $R(\omega)$ can be expressed as

$$R(\omega) = \frac{1}{\sqrt{1 - 14\omega^4 + \omega^8}}. \quad (3.10)$$

Alternatively, an approximate TPMS can be formulated by an implicit function, and each point on its surface has a constant value. The periodic surface φ in the approximate TPMS is expressed as

$$\varphi(r) = \sum_{k=1}^K A_k \cos \left[\frac{2\pi(h_k \cdot r)}{\lambda_k} + p_k \right] = C, \quad (3.11)$$

where r represents the position vectors in Euclidean space, A_k represents the amplitude factor, h_k is the k th grid vector in reciprocal space, which is a common vector

used in the concept of the reciprocal lattice, λ_k represents the periodic wavelength, P_k represents the phase offset, and C is a constant. General TPMS formulae represent the topologies of primitive, gyroid, and diamond TPMS, in which

$$\varphi(r) = \cos(X) + \cos(Y) + \cos(Z) = 0, \quad (3.12)$$

$$\varphi(r) = \sin(X) \cos(Y) + \sin(Z) \cos(X) + \sin(Y) \cos(Z) = 0, \quad (3.13)$$

$$\varphi(r) = \cos(X) \cos(Y) \cos(Z) - \sin(X) \sin(Y) \sin(Z) = 0, \quad (3.14)$$

where $X = 2\pi x$, $Y = 2\pi y$, and $Z = 2\pi z$.

The TPMS can be converted to a solid structure from a minimal surface to a periodic lattice based on two methods. In the first method, a TPMS solid lattice can be constructed by considering one of the subdomains divided by the minimal surface to be solid. In contrast, the other subdomain is considered void. Each of these subdomains can be considered a lattice of which volume fraction can be calculated by dividing the volume of the solid domain over the total volume. The other method uses a sheet network enclosed by two minimal surfaces evaluated at two different constants. Various parameters, such as periodicity and relative density, can be altered to tune the mechanical performance of the TPMS structures.

TPMS lattice structures possess advantages over strut-based topologies in terms of manufacturability and applicability in bone fixation. In particular, the continuous inclination angle of cell walls in TPMS structures can provide self-supporting features, which are suitable for the LPBF printing process. The three main types of TPMS and an I-graph-Wrapped Package graph (I-WP) lattice structures printed with Ti-6Al-4V have been studied to investigate their static and fatigue performance for bone-substituting applications (Bobbert et al. 2017). The diamond TPMS with a porosity of 60% and I-WP TPMS with a porosity of 44% can achieve a fatigue endurance limit of up to three times the previously developed AM bone substitutes. Meanwhile, the Ti-6Al-4V primitive pore geometry samples with three levels of porosity were fabricated by LPBF to investigate their mechanical properties (Soro et al. 2019). The mechanical properties of the best sample can achieve a Young's modulus of 22.3 GPa, yield strength of 160 MPa, and pore size of 596 μm .

The gyroid type of TPMS has also been reported to achieve a specific energy absorption almost three times greater than BCC structures for a given porosity level. Therefore, a gyroid TPMS structure was designed with varying volume fractions from 5% to 15% and printed through LPBF using Ti-6Al-4V powder (Yang et al. 2018b). The experimental uniaxial compression results confirmed that the center of the inclined struts was highly susceptible to fracture due to the stress concentrations and existing tensile stress of the upper surface resulting from bending deformation. Additionally, the fatigue properties of the LPBF-printed gyroid TPMS cellular structure were studied to evaluate its long-term performance in a dynamic bio-skeletal environment (Yang et al. 2020). The high-cycle fatigue results indicated that the fatigue ratio of the gyroid TPMS cellular structure reached 0.35 for the as-built samples and 0.45 for the sandblasted samples. These fatigue ratios were relatively

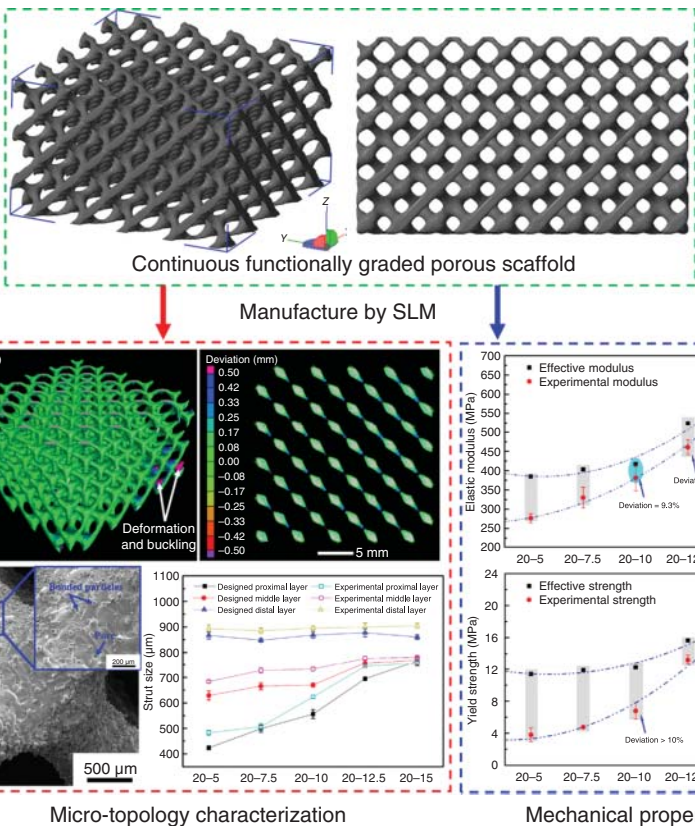


Figure 3.46 Continuous functionally graded porous titanium scaffolds manufactured by LPBF for bone implants. Source: Han et al. (2018b)/reproduced with permission from Elsevier.

high compared to most other bending-dominated lattice structures because of the smooth surface transitions between the struts.

The diamond TPMS has been studied to investigate the mechanical properties of the LPBF-printed parts. Functionally graded porous scaffolds (FGPSs) designed with the diamond unit cell over a wide range of grade volume fractions were printed by LPBF, as shown in Figure 3.46 (Han et al. 2018b). The experimental results indicated that the elastic modulus and yield strength of the LPBF-printed titanium FGPSs could be tailored to a range of 0.28–0.59 GPa and 3.79–17.75 MPa, respectively. Additionally, the effect of unit cell size on the printability, strut dimensions, stress and strain distributions, mechanical properties, and energy absorption capability of the diamond FGPSs was investigated (Yang et al. 2020). It was found from experiments and simulations that an increase in unit cell size reduces the Young's modulus and yield strength, which was attributed to the increase in the strut diameters and the geometric effect caused by the size of the unit cell.

The origami structure was inspired by the Japanese art of paper folding for decoration, and it is now a novel design strategy for ultralight and customizable

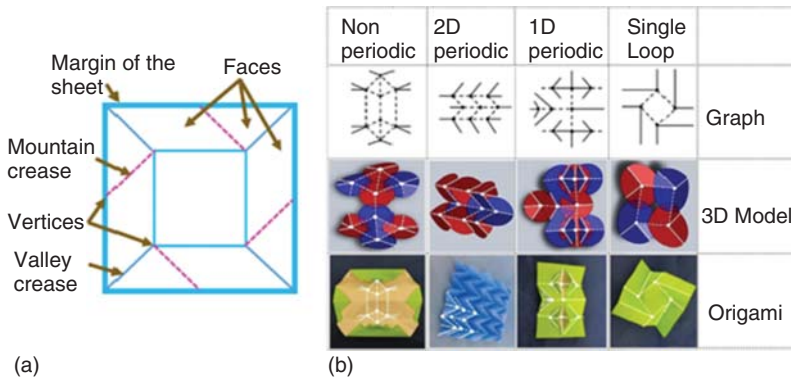


Figure 3.47 Fundamentals of origami-inspired metamaterials. (a) Schematic of a pin-wheel crease pattern illustrating the various origami concepts. Source: Reproduced from Peraza-Hernandez et al. (2014)/with permission of IOP Publishing Ltd. (b) Classification of action origami (i.e. origami models that exhibit motion in their final assembled state) in terms of the spherical mechanisms employed in nonperiodic, 2D periodic, 1D periodic, and single loop networks. Source: Bowen et al. (2013)/reproduced with permission from American Society of Mechanical Engineers.

mechanical metamaterials. Fundamentally, an origami structure is constructed by folding and assembling a planar material to form a three-dimensional structure. The final geometry depends on the number, order, and orientation of the folds that can be characterized by the creases and vertices (Figure 3.47).

Three classic origami patterns exist, namely, Miura-ori, nonperiodic Ron Resch, and square twist origami. Mathematically, the geometry of a simple periodically folded Miura-ori is a herringbone pattern consisting of identical unit cells of convex mountain creases and concave valley creases with four coordinated ridges. Vertices are formed when the four creases intersect, and four adjacent vertices bind congruent parallelograms arranged with inversion symmetry. The underlying mechanics of the 2D deformation of a Miura plate can be explained by the one-dimensional beam theory because the effective bending stiffness of its unit cell is singular in nature. Miura-based mechanical metamaterials exhibit negative in-plane Poisson's ratios and positive out-of-plane Poisson's ratios under deformation. The design parameters and mechanical properties of an LPBF-printed Miura-ori structure are presented in Figure 3.48 (Harris and McShane 2020). Vertical walls with variations in the angles in each layer form different design parameters for the design optimization of Miura-ori mechanical metamaterials.

3.8.3 Mechanical Metamaterials with High Shear and Bulk Moduli

Mechanical metamaterials with high shear/bulk moduli constitute two categories, i.e. vanishing shear modulus and negative-compressibility metamaterials. Vanishing shear modulus metamaterials include pentamode and Kagome structures. They are obtained when the shear modulus G approaches zero and the bulk modulus K is much greater than the shear modulus. The unique elastic modulus of these metamaterials represents an ideal type of flowing structure that is incompressible. The

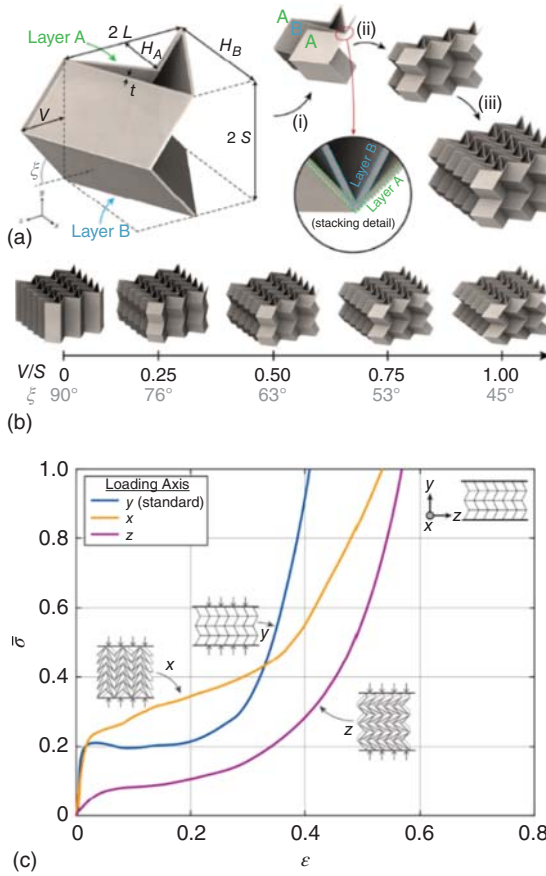


Figure 3.48 (a) Parameterization of a unit cell of the stacked Miura-ori design. (i)–(iii) Patterning of the unit cell to construct a cellular solid. (b) Variation of the stacked origami structure with increasing fold angle V/S as indicated in (a). (c) Normalized compressive stress–strain curves of the small thick-walled origami specimen tested in the three principal orientations. Source: Reproduced from Harris and McShane (2020)/with permission from Elsevier.

relationship between the parameters G , K , and the Poisson's ratio ν is defined as

$$\nu = \frac{3 - 2(G/K)}{2(G/K) + 6}. \quad (3.15)$$

The value of the Poisson's ratio is 0.5 for the vanishing shear modulus metamaterials because G is much smaller than K .

Pentamode metamaterials are the focus of this section, as they are more extensively studied than Kagome metamaterials in LPBF printing. Pentamode metamaterials exhibit an artificial structure that behaves like a fluid but has the form of a solid. It can support five modes of infinitesimal strain and only one mode of stress. The pentamode metamaterial has a diamond-shaped structure that can decouple mass transport and mechanical properties. For instance, the permeability of a pentamode-based bone scaffold can be adjusted without changing the mechanical properties (Figure 3.49).

As the unit cell of a pentamode metamaterial is formed by a center linkage point with four members arranged in a tetrahedron-like structure, four forces, F_0 , F_1 , F_2 ,

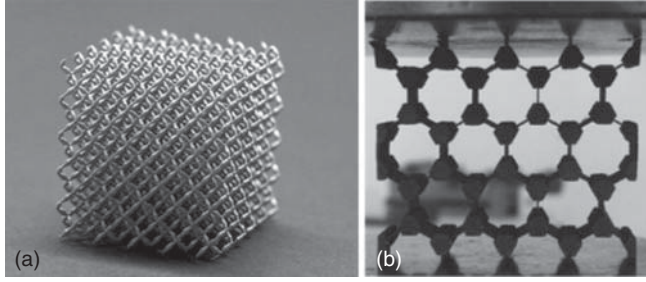


Figure 3.49 LPBF-fabricated mechanical metamaterials with vanishing shear modulus. (a) Pentamode metamaterial. Source: Hedayati et al. (2017)/reproduced with permission from AIP Publishing LLC. (b) Kagome metamaterial. Source: Zhang et al. (2019)/reproduced with permission from Elsevier.

and F_3 , are directed toward the members from the linkage point p . The corresponding elastic constants k_0 , k_1 , k_2 , and k_3 can be expressed as:

$$\begin{cases} F_0 = -k_0 p \\ F_1 = k_1(a_1 - p) \\ F_2 = k_2(a_2 - p) \\ F_3 = k_3(a_3 - p) \end{cases}, \quad (3.16)$$

where a_1 , a_2 , and a_3 are the selecting vectors representing the directional displacement in the unit cell. According to the balance of forces, the equations below can be obtained.

$$\begin{cases} kp = \sum_{i=1}^3 k_i a_i \\ k = \sum_{i=0}^3 k_i \end{cases}. \quad (3.17)$$

Following that, the linkage point p lies within the unit cell only if

$$0 < \frac{k_i}{k} < 1 \text{ for } i = 1, 2, 3, \quad (3.18)$$

while the integral of the stress within the unit cell is expressed as:

$$\sigma_i = \sum_{i=1}^3 k_i a_i \otimes a_i - kp \otimes p. \quad (3.19)$$

The fundamental idea behind pentamode metamaterials is that they only contain normal stress without shear elements in the stress tensors when the ratio of the integral stress and the prescribed stress is constant. Current applications for pentamode metamaterials include acoustic free-space cloaks, which can direct sound waves away instead of colliding with the cloaked object, thereby preventing detection. In addition to the acoustic cloaking application, pentamode metamaterials are suitable for developing ultrahigh strength-to-weight ratio structures.

Negative-compressibility metamaterials possess a range of elastic moduli that satisfy the following conditions: G exceeding zero and K being between $-4G/3$ and 0.

Negative linear compressibility (NLC) and negative area compressibility (NAC) materials are the two categories of negative-compressibility metamaterials, and their mechanical behaviors are investigated, through which the relative volume change of a solid or fluid is measured as a change in pressure. Negative thermal expansion (NTE) metamaterials are characterized by contraction upon heating. Among the few studies investigating NLC and NAC metamaterials through LPBF, the hexagonal and wine-rack-type honeycomb structures have been discussed with analytical and modeling methods (Grima et al. 2011). Nevertheless, NTE metamaterials are commonly developed using polymers instead of metals through LPBF because of their high coefficient of thermal expansion, which provides high functionality and deformability at varying temperatures.

3.8.4 Mechanical Metamaterials with Zero or Negative Poisson's Ratio

Most natural materials possess positive Poisson's ratios. In contrast, materials displaying auxetic behavior are usually counterintuitively described by a zero or negative Poisson's ratio (i.e. the ratio of the transverse to longitudinal strain). Mechanical metamaterials exhibiting such behavior are termed auxetic metamaterials. Under compression and tension along the axial direction, these metamaterials exhibit unconventional behaviors such as contraction and expansion along the transverse direction. The unusual behaviors of these auxetic metamaterials, including improved shear resistance, indentation resistance, fracture resistance, synclastic behavior, variable permeability, and energy absorption, have attracted extensive attention in research. Several representative types of auxetic metamaterials include re-entrant, double-arrowed, chiral, rotating square and triangle (Figure 3.50), missing rib, and origami and Kirigami structures (as mentioned in Section 3.8.2).

In general, the deformation mechanisms of auxetic metamaterials are categorized into three modes: bending-based, rotating-based, and bending-and-rotating hybrid modes.

Bending-based auxetic metamaterials, such as re-entrant structures (Figure 3.50a), consist of six plastic hinges and six connecting members in a unit cell. The auxetic behavior in compression is demonstrated by folding the diagonal ligaments around the plastic hinges that collapse the hourglass shapes into a densified rectangle stacked up by the ligaments (Yang et al. 2015). Similarly, the unfolding of the diagonal ligament transforms the hourglass shape into a hexagonal honeycomb shape, which eventually loses the auxeticity of the re-entrant structure. Similar deformation mechanisms are observed in the 3D re-entrant structures (Figure 3.50b).

The star-shaped re-entrant structure exhibits the same bending mechanism as the hourglass-shaped re-entrant structure (Figure 3.50c) (Grima et al. 2005). However, the hexagonal configuration of the star-shaped re-entrant unit cell provides a uniform deformation pattern at different angles compared to the hourglass-shaped re-entrant structure, which has the advantage of exhibiting anisotropic negative Poisson's ratio. The 2D double-arrowed auxetic structure, as depicted in Figure 3.50d, can achieve a high negative Poisson's ratio along a specific direction. The auxetic behavior of another type of re-entrant structure, the

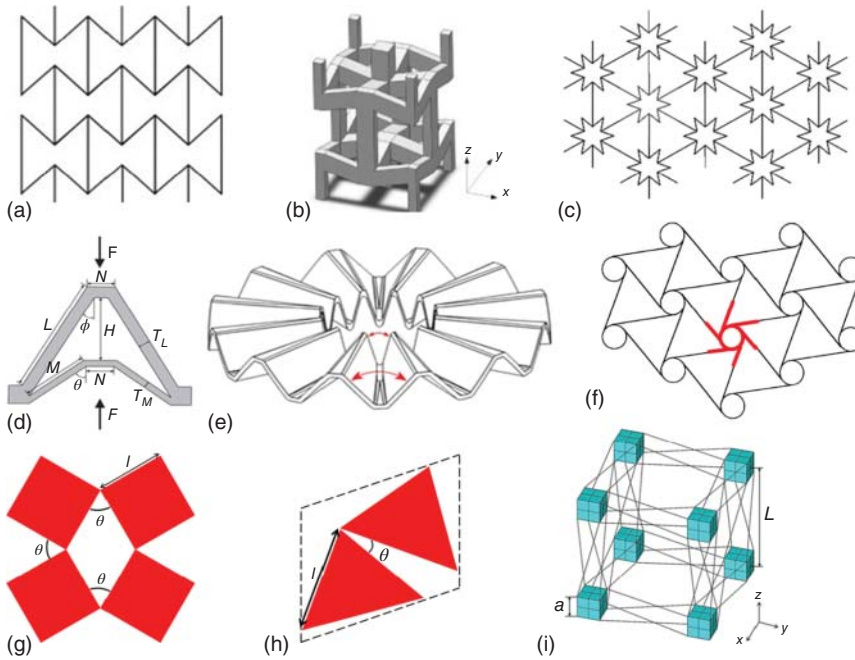


Figure 3.50 Geometrical designs for auxetic metamaterials. (a) 2D re-entrant structure, and (b) 3D re-entrant unit cell. Source: Reproduced from Yang et al. (2015)/with permission of Elsevier. (c) Star-shaped re-entrant structure. Source: Reproduced from Grima et al. (2005)/with permission of Taylor & Francis. (d) Double-arrowed unit cell, and (e) 3D double-arrowed structure. Source: Reproduced from Wang et al. (2016)/with permission of IOP Publishing. (f) Chiral structure. Source: Reproduced from Prall and Lakes (1997)/with permission of Elsevier. (g) Rotating square unit cell. Source: Adapted from Grima and Evans (2000). (h) Rotating triangle unit cell. Source: Reproduced from Grima and Evans (2006)/with permission of Springer Nature. (i) 3D chiral unit cell. Source: Reproduced from Ha et al. (2016)/with permission from IOP Publishing.

triangular re-entrant structure, is governed by its ability to fold or unfold the unit cell through bending deformations (Wang et al. 2016). It can achieve a very high anisotropic negative Poisson's ratio through optimization.

The rotating mechanism of auxetic metamaterials is represented by the rotating square (Figure 3.50g) (Grima and Evans 2000) and triangle unit cells (Figure 3.50h) (Grima and Evans 2006). Most studies have employed material removal methods (e.g. laser cutting) and other 3D printing methods (e.g. fused deposition modeling and selective laser sintering) to fabricate such structures. However, little literature reported on the usage of metal LPBF to produce these metamaterials exists. Hence, this type of auxetic metamaterial will not be detailed in this section.

A hybrid mechanism that combines bending and rotating is demonstrated by the chiral auxetics (Figure 3.50i). The term chiral structure is derived from the spinning nature of the structure, which is not mirror-symmetric but axisymmetric instead (Prall and Lakes 1997). A typical chiral unit cell is constructed by a center ring and ligaments. The ligaments are connected along the center ring's circumference

tangentially, equidistantly, and angled in a clockwise (or anticlockwise) direction. In general, three, four, or six ligaments are used to construct a chiral unit cell, and their structures are termed trichiral, tetrachiral, and hexachiral, respectively.

The hybrid mechanism displayed by chiral auxetic metamaterials is governed by the coupling of deformation via the bending of the ligaments and rotation of the center ring. When an external force is applied to the ligaments, the displacement of the ligaments induces a rotation of the center ring, which in turn induces the bending of the ligaments at the joints of the center ring. This interaction indicates that the hybrid mechanism can result in different negative Poisson's ratios. Hence, the targeted auxetic behavior of chiral or anti-chiral (i.e. containing ligaments oriented in both clockwise and anticlockwise directions) metamaterials can be achieved through the optimization of design parameters such as thickness, radius, and joint angles.

As shown in Figure 3.51a, a 2D missing rib, 2D re-entrant honeycomb, and 3D re-entrant honeycomb lattices were studied to investigate their mechanical responses under quasi-static and dynamic compression (Fila et al. 2017). The experimental results indicated that the LPBF-printed 316L structures with strain rate-sensitive material fillings, such as polyurethane, increased the specific energy absorption by 40%. Figure 3.51b shows the LPBF-fabricated 316L auxetic tubes, and their performance under low-impact conditions was studied (Lee et al. 2019). The results indicated that the auxetic tubes exhibited high specific energy absorption and low deceleration, which was caused by densification, as compared to conventional tubes and honeycomb tubes during crashing (Figure 3.51c).

3.9 Summary

LPBF is one of the most popular powder-based AM processes for printing metal parts. This chapter comprehensively introduces the critical aspects of LPBF, including the history, fundamentals, printing process, metallurgical defects, powder materials, equipment, representative microstructures and mechanical properties of the printed parts, and mechanical metamaterials. Among powder-based AM processes, LPBF utilizes small laser beam diameters and powder with small particle sizes, which enable the fabrication of complex metal parts with the highest part resolution and precise control of the energy input. However, the balling phenomenon and spattering occur during the LPBF process, and metallurgical defects, such as pores, cracks, and warpage, may be generated in the printed parts.

LPBF offers much freedom in the materials domain as it can process titanium and its alloys, aluminum alloys, nickel alloys, iron alloys, cobalt alloys, copper alloys, magnesium alloys, HEAs, etc. Furthermore, most materials can be solely printed by current commercialized LPBF machines developed by many commercial companies worldwide. However, multi-material printing through existing LPBF machines, especially for dissimilar materials, is still challenging for achieving part multifunctionality. In addition, there is a lack of a mature digital powder delivery system for

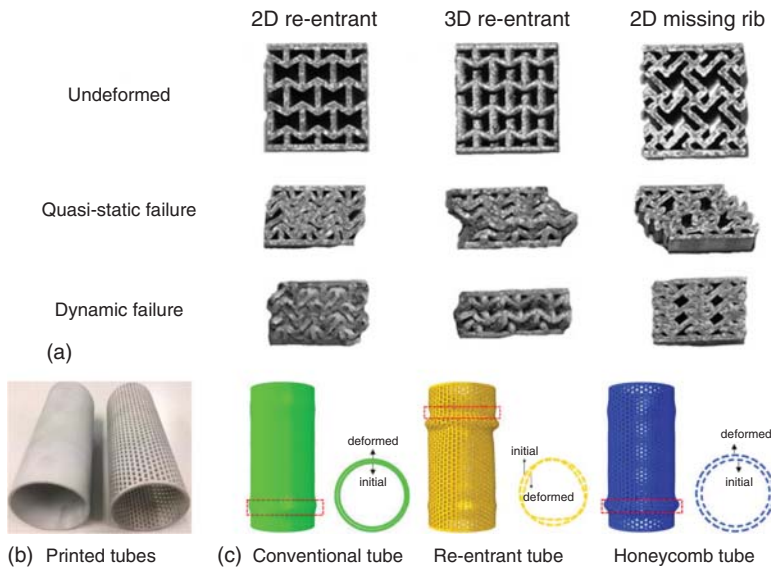


Figure 3.51 (a) Comparison of LPBF-printed auxetic metamaterials with 316L under quasi-static and dynamic loading: 2D re-entrant, 3D re-entrant, and 2D missing rib from left to right. Source: Fíla et al. (2017)/reproduced with permission from John Wiley & Sons. (b) LPBF-printed conventional tube and re-entrant tube, and (c) crash deformation profiles of LPBF-printed tubes: conventional tube, re-entrant tube, and honeycomb tube. Source: Lee et al. (2019)/reproduced with permission from Elsevier.

multi-material LPBF, along with issues such as material cross-contamination and low printing efficiency.

Typical LPBF machines are commonly equipped with a single laser and possess a limited building volume. However, a few leading companies, such as EOS, SLM Solutions, Bright Laser Technologies, and Laseradd, have developed large-scale machines equipped with multiple lasers and optics systems to increase the size of the printed parts and production efficiency. The flow of circulating inert gas within the build chamber and the synergistic incorporation of multiple lasers are critical technologies in large-scale printing. In addition, hybrid LPBF and subtractive manufacturing (LPBF aided by a subtractive system) can be developed to improve the surface quality of the printed parts.

Due to high cooling rates, LPBF-printed parts often exhibit fine microstructure and high mechanical strength compared to their counterparts fabricated by conventional processes. However, the low elongation is attributed to material brittleness and the porosity and microcracks within the materials. From the aspect of material design, the addition of lattice-matched nanoparticles to certain non-weldable powder materials (e.g. Al and Ni alloys) can effectively inhibit cracks and improve ductility by controlling solidification and equiaxed grain growth. Furthermore, additional energy sources, such as magnetic and ultrasonic fields, can be integrated into LPBF, i.e. multi-energy field LPBF, to reduce temperature gradients and residual stresses, minimize pores and cracks, and promote the growth of equiaxed grains.

In addition, the *in situ* monitoring of optics system parameters, powder-spreading on the powder bed, and melt pool characteristics can be integrated with the LPBF printing process to dynamically adjust the parameters through a feedback loop.

With the development of LPBF leaning toward the multi-material and multi-energy field printing of large parts with high efficiency and precision, more research efforts are expected to be dedicated to the process, thereby expanding its applicability within a broad range of industries.

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4

Electron Beam Melting

Electron beam melting (EBM) is a powder bed fusion process that employs an electron beam to selectively melt metal powder layers. This technology provides an alternative for processing materials that are either prone to cracking due to thermal stress or exhibit poor laser absorption during the laser powder bed fusion (LPBF) process. This chapter provides an overview of the history, fundamentals, processing characteristics, powder materials, equipment, microstructures, and properties of EBM-printed parts.

4.1 History

The patent for electron beam melting (EBM) was filed in 1993, which describes the principles of melting electrically conductive powder by an electron beam in a layer-by-layer manner to manufacture complex parts. The pioneering work on its development was conducted at Chalmers University of Technology, Sweden. In 1997, Arcam AB was founded, which further developed and commercialized the fundamental ideas underlying the patent, and the machine models were named EBM. The first commercial model, EBM S12, was released in 2002. Afterward, the company launched Arcam A2 in 2007, which was capable of producing large-scale parts for the aerospace industry.

Meanwhile, an important milestone was achieved in the orthopedic implant industry: Adler Ortho (Italy) released a Conformite Europeenne (CE) – certified Fixa Ti-Por hip implant fabricated through EBM in Europe. After this breakthrough, many CE-certified and Food and Drug Administration (FDA) – approved implants were produced using EBM. From 2009 to 2013, Arcam launched Arcam A1 and Q10 for the mass production of orthopedic implants, Arcam Q20 for the production of aerospace parts, Arcam A2X for processing high-temperature materials, and Arcam A2XX with the largest build chamber for large-scale production. In 2017, Arcam was acquired by GE Additive to further refine the technology for the mass production of metal parts.

4.2 Fundamentals

EBM schematically resembles laser powder bed fusion (LPBF). Since the energy source is an electron beam, the process is conducted in a vacuum (10^{-4} – 10^{-5} mbar) to prevent air from ionizing and deflecting the electron beam. This feature is highly advantageous for fabricating powder materials with a high affinity for oxygen (such as Ti–6Al–4V). Additionally, an elevated temperature (500–1100 °C) is maintained within the chamber to minimize residual stress. Therefore, the in-process distortion, warpage, and even cracking of the parts can be suppressed to a large extent, which is beneficial to printing materials prone to cold cracking, such as γ -TiAl. It can also process materials with high laser reflectivity and thermal conductivity, such as pure copper.

The schematic of an Arcam EBM system and its printing process is shown in Figure 4.1. The substrate plate is supported by a powder bed with a thickness of at least 40 mm for heat insulation to maintain the high building temperature and provide some tolerance for the expansion of the substrate during printing. The EBM process begins with heating the substrate plate to sinter the powder bed surrounding and below the substrate plate to prevent it from being shifted by the moving rake. The initial temperature is determined by the powder characteristics and regulated by the electron beam power. A layer of powder is delivered from the powder hoppers and then spread on the powder bed by the rake. Before melting each layer, the powder is preheated to a partial melting (termed pre-sintering in this chapter) status by rapidly scanning it with a defocused high-energy beam. After the powder layer is selectively melted, the building platform moves downward by one-layer thickness. A new layer of powder is delivered again, and the steps above are repeated until the part is completely printed. Afterward, the printed part is retained in the build chamber to cool it down to a specific temperature (usually set at ~ 200 °C). Next, helium gas is purged into the chamber to expedite cooling by convection until the part

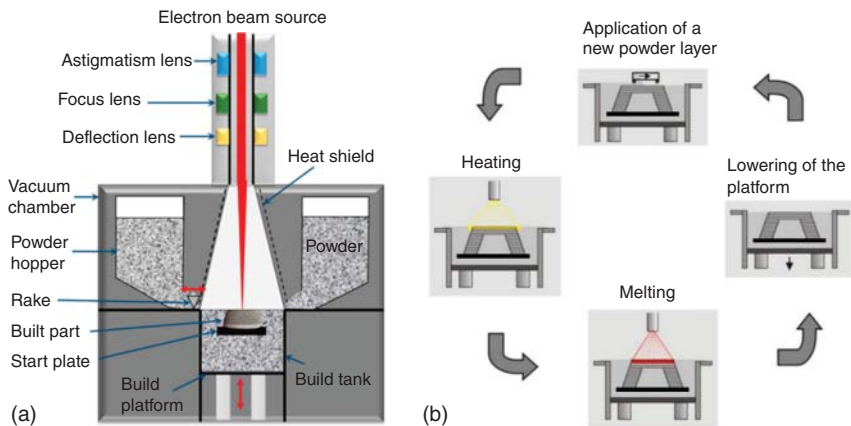


Figure 4.1 (a) Schematic illustration of an Arcam EBM system. Source: Reproduced from Galati and Iuliano (2018)/with permission from Elsevier. (b) Process for printing powder layers. Source: Reproduced from Körner (2016)/with permission from Taylor & Francis.

temperature is lowered below 100 °C, as the cooling rate decreases exponentially in this range if it is left to cool naturally in a high vacuum. After being retrieved from the build chamber, the printed part is covered by a soft agglomerate powder cake within the build tank and can be restored by sandblasting using the same powder.

More than 90% of the partially melted powder particles from the powder cake after printing can be recycled if their chemical composition and physical properties have been largely retained through proper control of the printing and recycling processes. The remaining partially melted powder particles are unrecyclable because they stick to form agglomerates, which can be removed by sieving in the powder recycling process.

The printing process consists of pre-sintering, melting, solidifying, and post-heating. To fabricate high-quality EBM parts, the following parameters must be optimized: beam current, focus offset, scanning speed, line offset, layer thickness, and scanning strategy. The beam current and focus offset determine the spot size, which can be as small as 0.1 mm (Biamino et al. 2011). The speed function index, which affects the instantaneous scanning speed, dynamically controls the translation of the electron beam and the melt pool size. Meanwhile, the line offset parameter regulates the hatch spacing, which is defined as the distance between two parallel lines of scanning.

The scanning pattern defines how the electron beam moves from one point to another. The most adopted scanning pattern is the zigzag pattern, in which the electron beam scans in a snake-shaped manner, and the scanning track is a series of parallel straight lines, which rotate by 90° for each printed layer (Figure 4.2a). The other scanning pattern is the contour pattern, in which the scanning track is a series of concentric lines that begin from the outermost line (Figure 4.2b).

The default scanning strategy combines the zigzag and contour patterns in each printing layer. It typically consists of three contour lines to trace the outer geometry of the part and zigzag lines to fill its inner area (Figure 4.2c).

At the pre-sintering stage, parameters such as the sintering temperature and powder conductivity are preset by the user to define the boundary conditions of the pre-sintering temperature. At the same time, the scanning speed, input current, and scanning strategy should be optimized. At the melting stage, numerous studies have been conducted to explore the optimization of process parameters for various alloys, particularly titanium alloys (Liu et al. 2016b, 2017; Zhao et al. 2016).

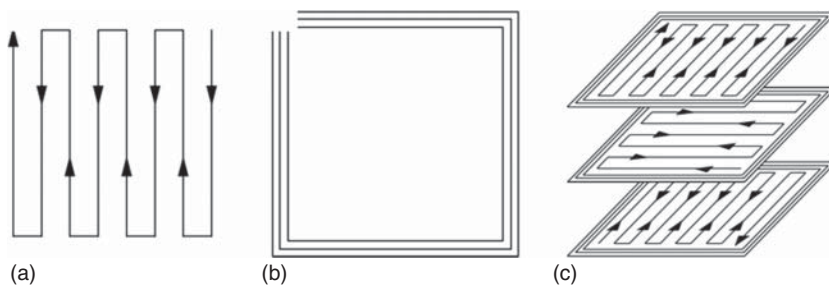


Figure 4.2 Typical scanning patterns used in EBM. (a) Zigzag pattern, (b) contour pattern, and (c) a combination of the two.

These process parameters can influence the size and depth of the melt pool and the thermal distribution, maximum temperature, and cooling rate of the alloys, which determine their densification, crystallographic textures, and mechanical properties. The cooling rates of the melt pool lie in the range of 10^3 – 10^5 K/s (Al-Bermani et al. 2010; Antonysamy et al. 2013), which are much lower than those of the LPBF process (typically in the range of 10^3 – 10^8 K/s). Since a fully molten stage is essential for fabricating completely dense parts, an adequate energy density of the input electron beam is required. However, it is difficult to convert the key process parameters, such as the focus offset and speed function, to the ones used in well-established classical energy formulae for LPBF processing. A trade secret of Arcam involves an auto-calculation energy-balancing algorithm embedded in the EBM system, which simultaneously adjusts a few interdependent parameters, such as the scanning speed and beam current, during the printing process. For example, the algorithm increases the scanning speed and beam current concurrently at the turning point of the zigzag pattern to avoid heat accumulation, which helps to improve the quality of the EBM-printed parts.

Each EBM process parameter exerts critical influences on the metallurgical defects (e.g. pores and cracks), microstructural features (e.g. phase and grain size), and surface characteristics (e.g. surface roughness) of the printed parts. Generally, optimizing the EBM process is challenging. At different stages of the layer melting process, many parameters are involved in developing the hatch and contour regions, as shown in Figure 4.3. For example, a contour design was optimized to improve the topographical and microstructural characteristics of the printed parts (Karimi et al. 2020). The scanning speed was established to be one of the most important parameters determining the surface roughness of one-contour parts. The beam current and focus offset influence the porosity of two-contour parts. Low porosity of the printed parts could be obtained by implementing a high beam current and

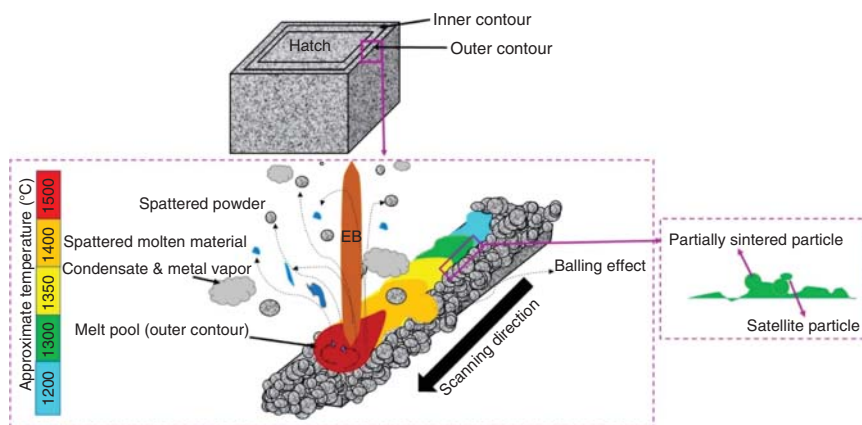


Figure 4.3 Schematic of various phenomena that occur during the EBM process. EB denotes the electron beam. Source: Reproduced from Karimi et al. (2020)/with permission from Elsevier.

a low focus offset, while the scanning speed and beam current could affect their geometrical characteristics.

The advantages of EBM are summarized as follows:

- The electron beam possesses an energy density a few times higher than a laser beam, which corresponds to greater penetration that promotes the uniform melting of highly reflective metals.
- The electromagnetic field generated by an electron beam unit can drive the electron beam to move at high transverse velocities (up to 10^5 mm/s for preheating and 10^4 mm/s for melting) within the printing area, thereby achieving a high build rate.
- The equipment can preheat the powder bed up to 1100°C to minimize the residual stress within the part, which is a recurring issue in LPBF that results in distortion and cold cracking of the printed part. This feature also enables EBM to possess the capability of *in situ* heat treatment.

Meanwhile, the limitations of EBM are:

- Because of larger powder particles and thicker printing layers, EBM-printed parts typically exhibit higher surface roughness than LPBF-printed components. The printed parts require extensive post-machining to achieve a smooth surface.
- The printing materials currently available for EBM are strictly restricted to non-magnetic metallic materials with high boiling points.
- EBM typically corresponds to lower dimensional accuracy and resolution than LPBF due to electron beams displaying larger spot sizes than laser beams. Thus, the minimum feature size of EBM is usually $\sim 500\ \mu\text{m}$.
- Loss of alloying elements frequently occurs during printing, especially for light elements with low boiling points (such as Al) in an ultrahigh vacuum environment.
- The equipment required for EBM is even more costly than that for LPBF.
- The selection of equipment manufacturers and commercially available powder materials for EBM is much more limited than that for LPBF, thereby impeding the research on EBM. Because of the multiple stages and numerous process parameters involved in EBM, it takes longer to develop new materials for EBM than for LPBF.

4.3 Preheating and Melting Processes

The EBM printing processes include pre-sintering and melting (i.e. contour melting and hatch melting). Before the melting process, the powder bed is uniformly pre-sintered by using a high-power defocused electron beam to rapidly scan each printing layer at a speed of ~ 10 m/s (Figure 4.4a). Meanwhile, the beam power is increased to ~ 3 kW (the recently developed machine model Arcam EBM Spectra H can provide up to 6 kW of power). Maintaining the predefined temperature in the building chamber and slightly pre-sintering the powder particles are critical for increasing their thermal and electrical conductivity. Process instabilities, such

as smoking due to the repulsion of charged powder particles, can be prevented by strictly monitoring the pre-sintering process, particularly for powder beds with large proportions of fine powder particles (Lodes et al. 2015). In addition, clusters of sintered powder particles can serve as supports for overhanging structures.

A high temperature stabilizes the powder bed through pre-sintering of the powder particles. The pre-sintering speed is influenced by the surface oxide layer on the powder particles. The high temperatures during pre-sintering play a significant role in determining the microstructure of a part and avoiding distortion and cracking by decreasing its residual stress. Compared to LPBF-printed parts, EBM-printed parts generally exhibit coarse grains due to a low cooling rate and residual stress due to a small thermal gradient.

After pre-sintering, the contours are melted in a quasi-multi-beam mode in which up to 100 points of each contour are quasi-simultaneously melted in a discontinuous manner. Such melting mode is achieved through the electron beam focus rapidly shifting from a point to another (Figure 4.4b), resulting in reduced surface roughness and improved accuracy of the geometry of the printed parts compared to those without contours. The melting procedure is typically performed by hatching (i.e. zigzag pattern). The powder particles are melted by the electron beam at a scanning speed of several meters per second in each printing layer (Figure 4.4c). During melting, the electrons collide with the powder particles, and most of the kinetic energy of the electrons is released in the form of thermal energy that sinters, fuses, and vaporizes the particles.

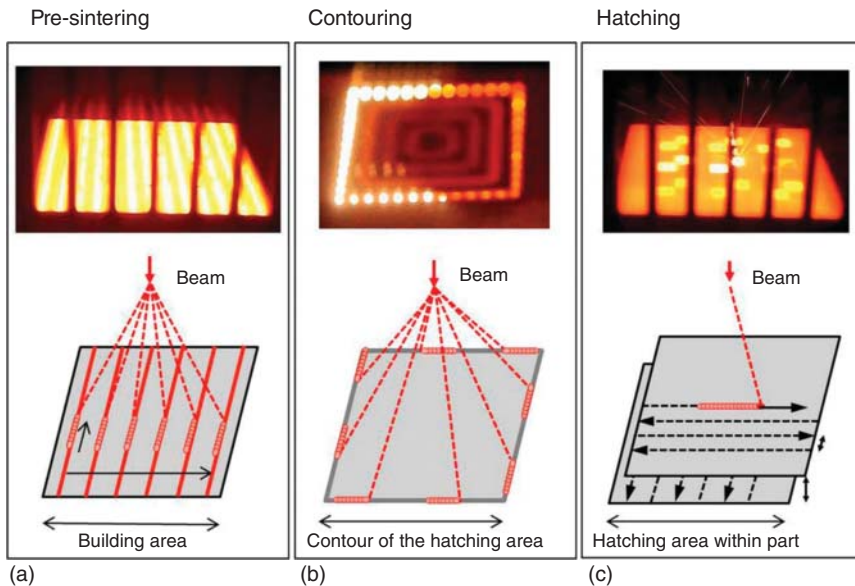


Figure 4.4 Pre-sintering and melting processes in EBM. (a) Pre-sintering by a quasi-multi-beam scan of the entire building zone with a defocused electron beam, (b) quasi-multi-beam contour melting, and (c) hatch melting. Source: Körner (2016)/reproduced with permission from Taylor & Francis.

Nevertheless, “smoking” of powder particles, also known as the pushing phenomenon, occurs in the form of an explosion. It can be caused by (i) the presence of water residue within the powder particles, which is vaporized in a volatile manner when the electrons collide with the powder, (ii) the momentum transferred from the electrons to the pre-sintered powder particles, which disrupts their cohesion, and (iii) the negative electrostatic charge of the powder particles, which leads to large mutually repulsive forces among them. The pushing phenomenon induced by the large momentum imparted by the electrons can be inhibited using larger powder particles. Meanwhile, the slight sintering of the powder particles increases their individual mass, which diminishes the effects of the repulsive forces, thereby reducing the occurrence of smoking.

Sintering of the powder particles occurs as a result of heat transfer during the pre-sintering and melting stages. The amount of heat transferred to the powder particles depends on the process parameters (e.g. the beam power, beam spot size, and scanning speed). When sufficient energy is absorbed by the material, the powder is melted and forms a melt pool. While EBM and LPBF share similar metallurgical processes, the vacuum environment in EBM lowers the boiling point and promotes the vaporization of lightweight elements (Biamino et al. 2011). Therefore, the composition of the raw powder, printed parts, and recycled powder of the two techniques is different.

The amount of energy released by the incident electrons is strongly related to the acceleration voltage, the atomic number of the constituent elements of the powder material, and the angle of incidence of the electron beam (Everhart and Hoff 1971). The released energy melts the powder particles and forms a melt pool that retains its molten state for a few milliseconds. The fluid dynamics parameters involved are primarily capillary forces and back pressure due to vaporization. To print fully dense parts, the depth of the melt pool should be much greater (about 3–4 times more) than the layer thickness to avoid interlayer bonding defects, namely, unmelted powder or non-connected layers.

Composition inhomogeneity results from the selective vaporization of elements with high vapor pressure. The uneven surface tension of the melt due to selective vaporization can cause material displacement and produce a melt surface with varying depths (Guo et al. 2015; Juechter et al. 2014) (Figure 4.5a). In these studies, the degree of composition inhomogeneity in EBM-printed parts depended on the scanning pattern. If the material displacement exceeds the layer thickness, applying a fresh powder layer cannot cover the protrusion of the solidified melt. When the next powder layer is melted, the material displacement will be aggravated if the scanning pattern is not changed (Figure 4.5b), which will eventually terminate the entire process. Elements such as aluminum and zinc exhibit extremely high vapor pressure, which significantly depletes these elements at the melt pool surface under high temperatures. The composition inhomogeneity due to element depletion can be partly mitigated by convection within the melt pool, but element segregation still occurs. As shown in Figure 4.5c, the distribution of aluminum varies across the different layers in an EBM-printed Ti–48Al–2Cr–2Nb alloy.

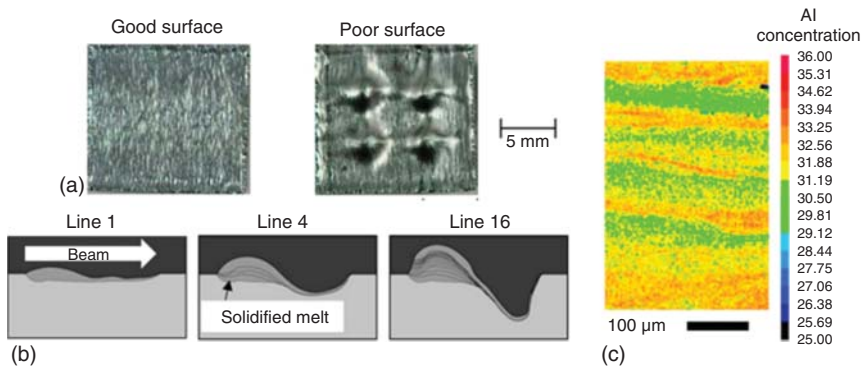


Figure 4.5 (a) Exemplary melt surface and poor melt surface caused by material displacement, (b) simulation results of melt displacement with the electron beam moving from left to right up to 16 times, and (c) element mapping representing the Al distribution in an EBM-printed Ti-48Al-2Cr-2Nb alloy. Source: Reproduced from Körner (2016)/with permission from Taylor & Francis.

A significant distinction between EBM and LPBF lies in the absorption of the beam energy. While incoming photons are absorbed within a depth of only several nanometers of the powder material, electrons can penetrate several micrometers of the powder surface before being absorbed. Consequently, EBM is more suitable for processing powder materials highly reflective to laser (e.g. pure copper and copper alloys).

4.4 Metallurgical Defects

In a controlled vacuum environment with optimized process parameters, parts printed by EBM can achieve a relative density of over 99.8%, which corresponds to a lower porosity level than LPBF products (Frazier 2014). However, since EBM and LPBF involve similar melting processes, metallurgical defects such as pores, delamination, and cracks are still present in EBM-printed parts.

Pores are a major defect in EBM-printed parts. They are formed through the residual gas trapped within the powder, lack of fusion, balling, keyhole formation from element vaporization, and uneven powder spreading. Wang et al. (2019) explored the printability of a CoCrFeMnNi high-entropy alloy (HEA) powder for EBM, and an image of the EBM-printed samples is shown in Figure 4.6a. Many powder particles were observed to be attached to the sides of the cuboid samples (Figure 4.6b), whose surface roughness R_a is 41.1 μm. Figure 4.6c presents the morphology of the top surfaces of the samples with different extents of protrusion and numbers of lack-of-fusion pores. The protrusion resulted from turbulent melt pool motion, which was driven by strong forces induced by temperature gradients, Marangoni convection, and evaporation.

To maintain the same fusion condition throughout the different regions of a part, it is necessary to dynamically adjust the line and focus offset, scanning

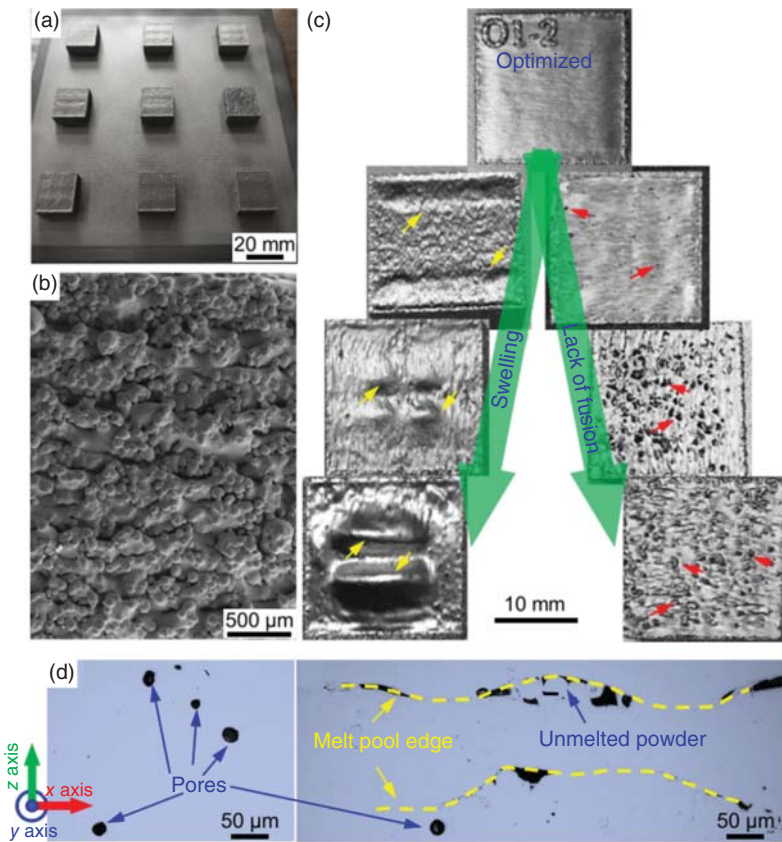


Figure 4.6 (a) EBM-printed HEA samples and (b) SEM image of a rough sample surface along the z direction. (c) Top surfaces of the cuboid samples. The yellow and red arrows indicate protrusion and lack-of-fusion pores, respectively. (d) Optical microscope (OM) images displaying the pores. Source: Reproduced from Wang et al. (2019)/with permission from Elsevier.

speed, reference current, and pre-sintering temperature, which is achieved by the auto-calculation algorithm. For example, a combination of large line offsets, high scanning speeds, and low reference currents can lead to shallow melt pools and low building temperatures; a large focus offset can broaden the width of the melt pools. However, the resultant low input energy will be inadequate to form melt pools that are sufficiently deep (Figure 4.6d). In general, there are two types of pores, namely, irregular pores and spherical pores. Once a melt pool cannot penetrate the previously solidified layer, a lack-of-fusion region may occur with the presence of some unmelted powder particles, resulting in irregular pores. During the rapid solidification process, spherical pores are formed from gas bubbles that have previously been trapped within the powder particles. As the EBM process is performed in a vacuum environment, the presence of gas mainly originates from inert gases, such as argon, trapped in the raw powder during the atomization process (see Chapter 1).

Generally, a two-dimensional (2D) metallographic method is employed to analyze the size and distribution of pores in EBM-printed parts. Recently, X-ray characterization techniques, such as micro-computed tomography (micro-CT), have been utilized to visualize the pore distribution in three-dimensional (3D) materials. For example, by performing micro-CT scans of EBM-printed Ti-6Al-4V parts, it was found that the distribution of defects mainly depends on the scanning strategies (Tammam-Williams et al. 2015).

Compared to LPBF-printed components, EBM-printed components possess low residual stress levels due to the high building temperature (500–1100 °C) in the building chamber during the printing process. For example, using the neutron diffraction technique, the residual stress in Inconel 718 produced by EBM was much lower than that by LPBF (Sochalski-Kolbus et al. 2015). Minor residual stress was also observed in an EBM-printed Ti-6Al-4V alloy (Hrabe et al. 2017).

Cracking is another concern for EBM-printed parts, particularly for non-weldable alloys. In a study by Chauvet et al. (2018), intergranular hot cracking was identified in an EBM-printed non-weldable Ni-Co-Cr-Mo-Al-Ti-B nickel-based superalloy, as shown in Figure 4.7. An investigation of its underlying mechanism reveals that crack formation in the superalloy parts requires the presence of liquid films, and the occurrence of hot cracking is determined by the degree of grain boundary misorientation. The grain boundary energy values of high-angle grain boundaries (HAGBs) and low-angle grain boundaries differ significantly, which affects the stability of the liquid film. Cracking preferably occurs in HAGBs due to their large grain boundary energy values that can stabilize the liquid film. Moreover, the local enrichment of trace elements, particularly boron, plays an important role in stabilizing the liquid film at temperatures lower than its theoretical equilibrium solidus temperature. Although hot cracking occurs in the presence of a liquid film and large thermal stress, it has been demonstrated that the thermal stress within an EBM-printed non-weldable nickel-based airfoil can be redistributed by optimizing the scanning strategy (Lee et al. 2020). Other scanning strategies, such as random raster scanning and spot melting, can mitigate cracking or distortion within EBM-printed parts.

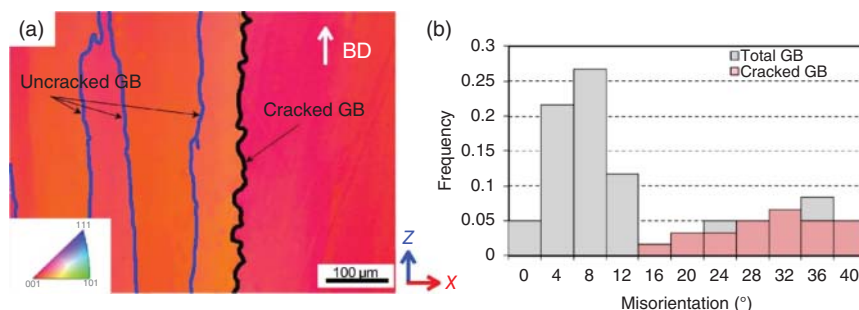


Figure 4.7 (a) Electron backscatter diffraction map indicating cracks propagating along the high-angle grain boundaries ($>15^\circ$ in black). Low-angle grain boundaries are delineated in blue ($5^\circ < \text{angle} < 15^\circ$). (b) Histogram displaying the distribution of the grain boundaries (gray). The distribution of the cracked grain boundaries is delineated in red. Source: Reproduced from Chauvet et al. (2018)/with permission from Elsevier.

The surface roughness and near-surface defects are primary features in the contour zones of printed layers. Generally, the high surface roughness of EBM-printed parts, particularly those with inclined geometrical features, leads to high stress concentration and subsequent crack initiation. The surface defects of the printed parts include partially melted particles located near the surface and some irregularly shaped melted particles generated from the powder bed being sputtered by electrons, which occurs when the electron beam possesses a high energy density. Because of such undesirable surface features, most EBM-printed parts require post-processing to improve their surface quality.

4.5 Powder Materials

Before optimizing the process parameters for EBM, the powder should be characterized to determine its suitability. An ideal powder should exhibit good flowability ($<25\text{ s}/50\text{ g}$, similar to Arcam's supplied powder), high apparent density (over 50% of the density of the bulk material), no internal pores from the production process, and no fine particles ($<10\text{ }\mu\text{m}$). Generally, pre-alloyed powders produced through gas atomization or the plasma rotating electrode process are used in EBM. The powder particles are spherical, and the standard particle sizes are in the range of $45\text{--}100\text{ }\mu\text{m}$. The possibility of using powders with smaller particle sizes ($25\text{--}45\text{ }\mu\text{m}$) in EBM was investigated (Karlsson et al. 2013), and no significant distinction between the properties of the parts printed using standard powders and powders with smaller particle sizes were observed. However, the latter possesses the potential to improve the surface quality of the printed parts. It was suggested that the material of the substrate should be identical or similar to that of the powder because it prevents contamination and ensures proper bonding.

Powders can be recycled and reused in the EBM process. The effect of the number of powder recycling cycles on the properties of Ti-6Al-4V powder was examined (Tang et al. 2015a), which revealed that the particle size distribution became narrower with an increase in the number of recycling cycles. Additionally, the powder particles were rougher and less spherical. However, the flowability of the powder was found to increase after each cycle. Although the main characteristics of the powder underwent minor changes after each cycle, no powder spreading/smoking was observed after 21 cycles. Nevertheless, recycling a powder increases its oxygen content, which improves the yield strength and ultimate tensile strength of the printed parts.

Commercialized materials for Arcam EBM include Ti-6Al-4V, Ti-6Al-4V ELI, commercially pure titanium, F75 Co-Cr-Mo, Inconel 718, pure titanium, pure copper, highly alloyed tool steel, and TiAl. Based on the currently limited selection of materials available for EBM compared to LPBF, extensive studies have been conducted to explore and develop other materials for EBM, such as Fe-based, Ni-based, and Ti-based alloys, HEAs, and their composites. A summary of these materials is presented in Table 4.1.

Table 4.1 Summary of commercialized and experimental powder materials for EBM.

Material group	Materials	Commercial materials from Arcam
Ti-based	Pure Ti, Ti-6Al-4V, Ti-6Al-4V ELI, Ti-24Nb-4Zr-8Sn, TA15, Ti-Nb, Ti-Mo, Ti-Nb-Ta-Zr	Ti-6Al-4V, Ti-6Al-4V ELI
Fe-based	Pure Fe, 316L, H13, Cr-Mn-Ni TRIP steel, Fe-18Cr-2W-0.5Ti-0.3Y ₂ O ₃	Highly alloyed tool steel
Al-based	Al-Si10-Mg	—
Ni-based	IN718, IN625, Haynes 282, CMSX-4, K417, Rene 142, Rene-N5, 713ELC	IN718
Co-Cr-based	Co-Cr-Mo, Co-Cr-Ni-W	Co-26Cr-6Mo-0.2C
TiAl	Ti-47Al-2Cr-2Nb, Ti-48Al-2Cr-2Nb, Ti-45Al-7Nb-0.3W	Ti-48Al-2Cr-2Nb
Pure metals	Ti, Cu, Nb, Fe, W	Ti, Cu
HEAs	CoCrFeMnNi, AlCoCrFeNi, CoCrFeNiTiMo, AlCrMoNbTa	—
Others	NiTi, Cu-25Cr composites, 35 wt.% NiBSi + 64 wt.% WCp composites	—

4.6 Equipment

An EBM system generally consists of an electron beam unit, a vacuum chamber, a powder feeder system, and a computerized control system (Figure 4.1). The electron beam module comprises an upper column for electron generation and a lower column that contains magnetic lenses for beam formation and deflection. In the upper column, a hot tungsten filament or a lanthanum hexaboride cathode emits electrons under a voltage of ~ 60 kV, and the beam current is in the range of 1–50 mA. In contrast to an electron beam generated by a tungsten filament, a beam generated by a lanthanum hexaboride cathode has high quality. However, the cathode is more susceptible to “smoking”. Therefore, it is only used for titanium processing. The lower column of the electron beam module includes astigmatism lenses, focus lenses, and deflection lenses, which control the shape, size, and position of the beam on the substrate, respectively.

The vacuum chamber consists of a build container, a powder feeder, and a raking system. The platform of the build container can move along the z axis, and it includes a processing platform for preheating and printing. Two hoppers for powder storage are available, and the powder is fed to the chamber plate by gravity. The raking system controls the degree of spreading of the powder, which forms layers with a thickness of 0.05–0.2 mm during printing. The process is conducted in a vacuum environment (10^{-4} – 10^{-5} mbar) to prevent air from interfering with the electron beam. In addition, helium gas is typically purged to the chamber with a low pressure of 10^{-3} mbar to neutralize the negative charges on the powder particles, thereby preventing electrostatic charging and smoking, which may result in process termination.

Currently, the supply of commercialized EBM equipment is dominated by Arcam, which was acquired by GE Additive in 2017. Commercialized EBM machines

Table 4.2 Summary of the specifications of EBM machine models produced by Arcam.

Equipment	Build volume (mm ³)	Beam power (kW)	Process temperature (°C)	Machine size (D × W × H) (mm ³)	Materials
Arcam EBM Q10plus	200 × 200 × 180	3	—	1066 × 2060 × 2608	Ti–6Al–4V, CoCr, pure Ti, pure Cu
Arcam EBM Q20plus	Ø 350 × 380	3	—	1300 × 2400 × 2945	Ti–6Al–4V
Arcam EBM A2X	200 × 200 × 380	3	600–1100	900 × 1850 × 2200	Ti–6Al–4V, Ni 718, TiAl
Arcam EBM Spectra H	Ø 250 × 430	6	600–1100	1328 × 2344 × 2858	Ti–6Al–4V, Ni 718, highly alloyed tool steel
Arcam EBM Spectra L	Ø 350 × 430	4.5	700	1328 × 2344 × 2858	Ti–6Al–4V, pure Cu

include Arcam EBM Spectra L, Arcam EBM Spectra H, Arcam EBM Q10plus, Arcam EBM Q20plus, and Arcam EBM A2X, and their specifications are summarized in Table 4.2. The acquisition of Arcam by GE has enhanced the core competency of EBM in orthopedic and aerospace applications, with over 100 000 clinical evaluations and FDA-approved hip implants being produced as of 2018 and over 250 TiAl turbine blades being installed in each Boeing 777X aircraft engine (GE9X) in 2019. In addition, during 2018–2019, EBM systems Spectra H and Spectra L were released, which featured increased power, larger build volume, improved productivity, a closed powder-handling system, and an automatic beam calibration function. In 2019, GE Additive opened its 15 000 m² Arcam EBM Center of Excellence in Gothenburg, Sweden, to boost its production capacity and R&D efforts to meet the ever-increasing demands for EBM-printed components.

Other representative commercial companies that are developing/have developed EBM systems are Sailong (S200 Production EBM 3D Printer and Y150 Biomedical EBM 3D Printer) and QBEAM (QbeamLab, QbeamMed, and QbeamAero) of China, Freemelt (Freemelt ONE) of Sweden, and JEOL (JAM-5200EBM) of Japan. Some research groups have also attempted to develop their respective EBM systems. For instance, the *iwb* application center (Germany) developed an EBM system with an electron beam power of 10 kW by modifying an existing electron beam welding system.

4.7 Microstructures and Mechanical Properties

In general, EBM is performed at high building temperatures (e.g. 300 °C for pure copper, 600 °C for Ti, and 1100 °C for TiAl), which significantly affect the microstructures and mechanical properties of the printed parts. Additionally, the mechanical properties of the parts are height-dependent as a result of the *in situ*

heat treatment conditions during the printing process. After the final solidification of the first printed layer, the building temperature measured by the thermocouple placed underneath the substrate plate fluctuates significantly. A fixed building temperature can only be achieved after 10–20 layers are printed. The region near the melting surface approaches the solidification temperature of the printed material several times during the printing process, and the material may undergo several rounds of phase transformation.

With an increase in the number of printed layers, their solidification is influenced by complex thermal cycles. The preheating process in EBM results in a consistently high temperature throughout the printed parts, which eliminates residual stress within them and endows them with a good combination of strength, plasticity, and performance homogeneity. Because of their refined microstructures, EBM-printed parts exhibit mechanical properties comparable to or superior to their wrought counterparts. However, their strength is generally inferior to that of their counterparts printed by laser powder bed fusion and laser-based directed energy deposition.

4.7.1 Titanium and Its Alloys

Presently, titanium and its alloys, which are considered difficult-to-machine materials in conventional manufacturing, are mostly utilized for EBM. The processibility of these materials with EBM has been extensively verified for $(\alpha + \beta)$ -type and β -type titanium alloys.

Ti-6Al-4V is an $(\alpha + \beta)$ -type titanium alloy comprising 6 wt.% Al (an α -stabilizing element), 4 wt.% V (a β -stabilizing element), and other interstitial elements such as O. A representative printed Ti-6Al-4V sample, as shown in Figure 4.8, consists

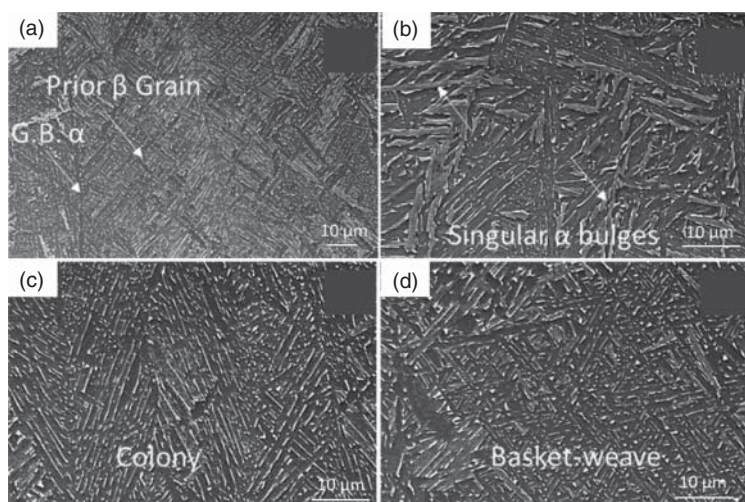


Figure 4.8 SEM images of the microstructures of EBM-printed Ti-6Al-4V samples. (a) Columnar prior β grains, (b) singular α bulges, and $(\alpha + \beta)$ microstructures with (c) colony and (d) basket-weave morphology. G.B. denotes a grain boundary. Source: Tan et al. (2015)/reproduced with permission from Elsevier.

of (i) columnar prior β grains which are delineated by α grain boundaries and (ii) a transformed α/β microstructure with the Widmanstätten pattern and lamellar colony, as well as singular α bulges, within the prior β grains. The formation of the α grain boundary along the grain boundaries of the prior β grains indicates the β -to- α phase transformation of the sample. Consequently, the microstructure formed in an EBM-printed Ti-6Al-4V sample differs from that of an LPBF-printed Ti-6Al-4V sample, in which the martensitic α' phase is commonly present as a result of transformation from the β phase.

In a study by Guo et al., α' martensite was only observed near the surface of an EBM-printed Ti-6Al-4V sample, implying that the prior β phase first transforms into the martensitic α' phase before decomposing into $(\alpha + \beta)$ phases (Guo et al. 2015). The thickness of the α -lamellae was found to be dependent on the energy input, building temperature, and cooling conditions. In another study by Scharowsky et al., the thickness of the α -lamellae of a Ti-6Al-4V sample was observed to increase with the energy input and building temperature. However, the yield stress decreased as a result (Scharowsky et al. 2015).

Generally, the cooling rate of an EBM-printed product decreases with the building height, thereby resulting in an anisotropic microstructure along its height. For example, in a related study, an equiaxed-to-columnar transition of the prior- β grains in an EBM-printed Ti-6Al-4V sample was observed to occur as the number of build layers increased. Such a transition was accompanied by an increased thickness of the retained rod-like β phase (Figure 4.9) (Tan et al. 2015). It was suggested that the relatively high heat conductivity of the substrate had led to a high degree of super-cooling, resulting in the equiaxed-to-columnar transition of the grain morphology. The mechanical properties of the printed parts vary within them due to the height dependence of local thermal conditions.

The mechanical properties of EBM-printed Ti-6Al-4V alloys are summarized in Table 4.3. With optimized process parameters, EBM can produce parts possessing strength and elongation comparable to those of the wrought products (Murr et al. 2009). A decrease in the thickness of the α lamellae corresponds to an increase in the mechanical strength of the printed parts according to the Hall-Petch relationship. EBM-printed Ti-6Al-4V parts with smaller grain sizes and thinner α lamellae can exhibit enhanced tensile strength. Post-heat treatment (e.g. hot isostatic pressing [HIP]) of the printed parts above the β transus temperature resulted in the desired acicular or Widmanstätten morphology. As the size of small EBM-printed Ti-6Al-4V parts increases, their strength decreases, and their ductility increases, which has been attributed to the increase in the thickness of the α lamellae. EBM-printed Ti-6Al-4V parts were found to exhibit slightly lower yield strength along their height than across the building plane, which may be explained by their anisotropic microstructures and the metallurgical bonding defects between the layers (de Formanoir et al. 2016).

The presence of nonspherical lack-of-fusion pores, which contain unmelted or partially melted particles, is detrimental to the mechanical properties of the printed parts with respect to the x - y plane due to the sharp edges of the pores acting as stress risers when the applied tension is perpendicular to the z direction. Consequently, the

Equiaxed-to-columnar grain transition

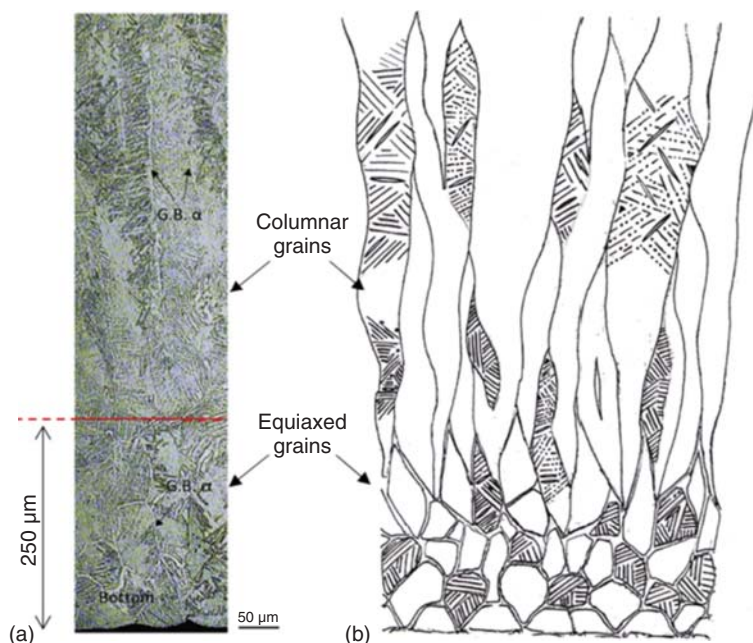


Figure 4.9 (a) OM image and (b) schematic representing the equiaxed-to-columnar transition of prior β grains in an EBM-printed Ti-6Al-4V alloy. Source: Reproduced from Tan et al., (2015)/with permission of Elsevier.

Table 4.3 Summary of the mechanical properties of EBM-printed Ti-6Al-4V alloys.

Ultimate tensile strength (MPa)	Yield strength (MPa)	Elongation (%)	Young's modulus (GPa)	Hardness (GPa)
950–990 ^{a)}	910–940	14–16	120	—
910 ^{b)}	830	—	118	3.21
1100–1400 ^{c)}	—	12–25	—	4.3
1150–1200 ^{d)}	1100–1150	16–25	—	3.6–3.9
994–1029 ^{e)}	883–938	11.6–13.6	—	—
930 ^{f)}	865	12–17	—	—
945–965 ^{g)}	823–852	13.2–16.3	—	3.19–3.27
990–1180 ^{h)}	900–1100	18–23	—	—

a) Parthasarathy et al. (2010)

b) Facchini et al. (2009)

c) Gaytan et al. (2009)

d) Murr et al. (2009)

e) Al-Bermani et al. (2010)

f) Scharowsky et al. (2015)

g) Tan et al. (2015)

h) Zhao et al. (2016).

printed samples subjected to tension perpendicular to the z direction exhibited 28% lower elongation than those subjected to tension along the z direction.

Another titanium alloy extensively investigated for EBM is the β -type Ti-24Nb-4Zr-8Sn (Ti2448) alloy, which was developed for biomedical applications because of its low Young's modulus and high tensile strength (Hao et al. 2007). Such excellent properties were attributed to the α -phase precipitates located at the β grain boundaries due to high-temperature preheating, as shown in Figure 4.10 (Liu et al. 2016a). The microstructure of EBM-printed parts can also facilitate fatigue crack deflection in their columnar grain regions (Liu et al. 2017). In this study, Ti2448 porous structures with a porosity of 70% were discovered to exhibit excellent mechanical properties, with a strength-to-modulus ratio over twice that of Ti-6Al-4V porous structures with the same porosity (Liu et al. 2016b). Additionally, the Ti2448 porous structures displayed high normalized fatigue strength due to their super-elastic properties and large plastic regions at their fatigue crack tips.

There are generally four types of TiAl microstructures, namely, the near- γ , duplex lamellar, near-fully lamellar, and fully lamellar structures. Owing to their low density, high specific yield strength, high specific stiffness, and favorable creep properties at elevated temperatures of 600–900 °C, γ -TiAl alloys are highly adopted in various industrial applications. For example, commercialized γ -TiAl alloys have been employed to manufacture the low-pressure turbine blades of GEnx engines that power the Boeing 787 and 747-8 aircrafts.

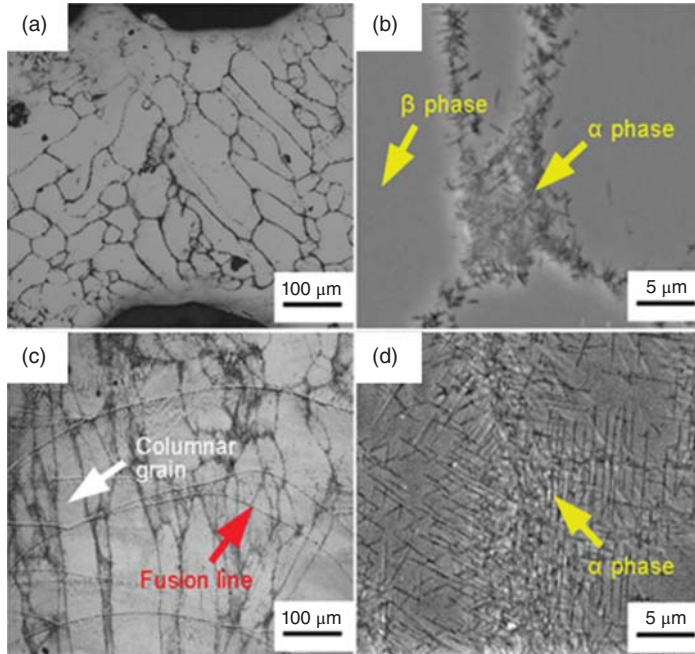


Figure 4.10 Microstructure of an EBM-printed Ti2448 alloy. (a) OM and (b) SEM images taken perpendicular to the z direction. (c) OM and (d) SEM images taken along the z direction. Source: Liu et al. (2016a)/reproduced with permission from Elsevier.

TiAl is favorably processed by EBM because the building temperature can reach up to 1100 °C. Therefore, crack formation is eliminated within the printed parts, which commonly occurs during the LPBF process because the ductility of TiAl is insufficient to counteract the high thermal stress during the rapid solidification process (Tang et al. 2015b). An EBM-printed γ -TiAl alloy was found to exhibit equiaxed small grains ($\sim 2\mu\text{m}$) with lamellar $\gamma/\alpha_2\text{-Ti}_3\text{Al}$ colonies displaying an average spacing of $0.6\mu\text{m}$ and a microhardness of 4.1 GPa (Murr et al. 2010). However, Al evaporates significantly during the printing process because of its low melting point. An EBM-printed Ti-48Al-2Cr-2Nb alloy was reported by Biamino et al. to undergo 1 wt% Al vaporization (Biamino et al. 2011). The as-built alloy possessed an extremely fine microstructure (Figure 4.11a), but full recrystallization in near-equiaxed grains with sizes smaller than $20\mu\text{m}$ was obtained after HIP, as shown in Figure 4.11b,c. Subsequent heat treatment at 1320 °C for two hours resulted in a duplex microstructure containing $\sim 40\text{ vol.}\%$ of a lamellar phase with an average grain size of $\sim 100\mu\text{m}$ surrounded by fine equiaxed grains (Figure 4.11d). Consequently, the yield strength, ultimate tensile strength, and elongation of the treated alloy at room temperature were measured to be $\sim 350\text{ MPa}$, $\sim 470\text{ MPa}$, and 1%, respectively. At high temperatures (500–800 °C), its elongation was increased to beyond 5% without significantly sacrificing its strength.

The as-built γ -TiAl alloys exhibit a higher fatigue threshold and strength than their counterparts produced through conventional processes, such as casting and powder metallurgy. Post-heat treatment is often necessary to further refine the microstructure and mechanical properties of the as-printed components.

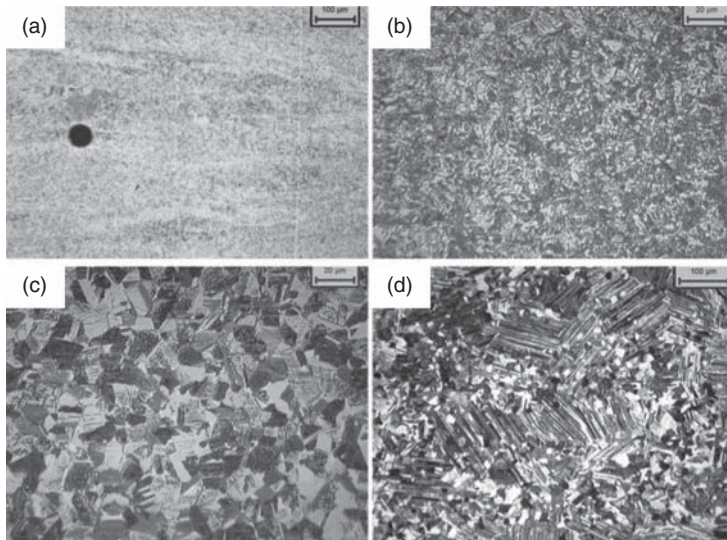


Figure 4.11 (a) Representative spherical pore defect in an EBM-printed γ -TiAl alloy and microstructures (b) of the as-printed alloy, (c) after HIP, and (d) after heat treatment. Source: Biamino et al. (2011)/reproduced with permission from Elsevier.

Nevertheless, TiAl alloys are still inferior to nickel-based alloys in terms of fatigue crack growth resistance, ductility, and fracture toughness.

4.7.2 Nickel Alloys

Nickel-based alloys can be categorized into weldable and non-weldable types. Non-weldable alloys are difficult to process by EBM and LPBF as most contain a substantial proportion of the γ' phase, which strengthens the alloy but renders it highly prone to cracking. Among weldable nickel-based alloys, Inconel 625 and Inconel 718 have been extensively explored for EBM processing. Inconel 625 is widely utilized in columnar-grained gas turbines because of its high Cr content, strength, processability, and corrosion resistance.

Figure 4.12 shows the representative microstructures of EBM-printed Inconel 625 and Inconel 718 parts (Murr et al. 2011; Körner 2016). Figure 4.12a shows equiaxed grains in the horizontal plane of the printed Inconel 625 alloy (Murr et al. 2011). Precipitates (indicated as black) could be observed on both the boundaries and interiors of the grains. The black precipitates along the grain boundaries were considered to be of the γ' phase. Comparatively, columnar grains could be found in the vertical plane of the printed alloy (Figure 4.12b). The EBM-printed Inconel 718 alloy often consisted of a face-centered-cubic (FCC) γ -matrix strengthened by several phases

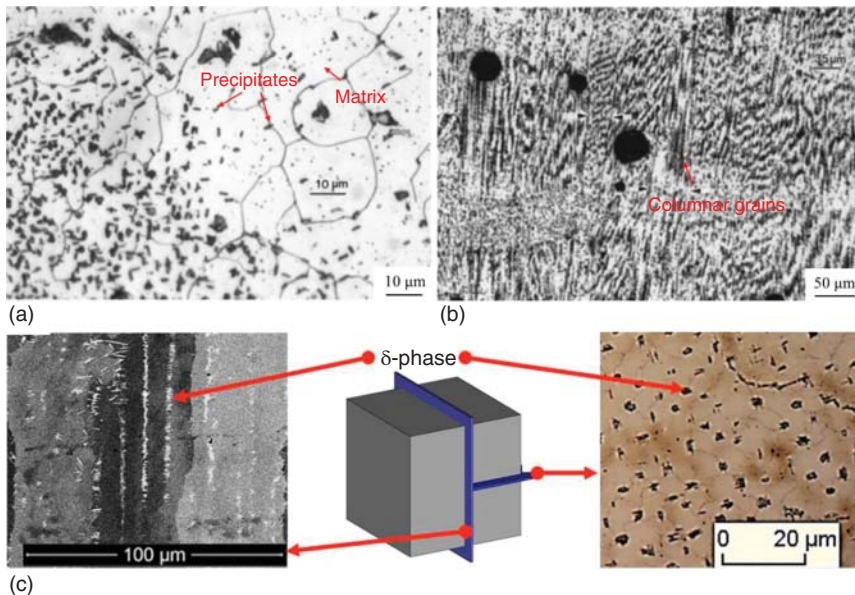


Figure 4.12 OM images of the microstructure of an EBM-printed Inconel 625 alloy. (a) Equiaxed grains and precipitates in the horizontal plane and (b) columnar grains in the vertical plane. Source: Murr et al. (2011)/reproduced with permission from Springer Nature. (c) δ -phase precipitation in the interdendritic zones with columnar architecture in an EBM-printed Inconel 718 alloy. Source: Körner (2016)/reproduced with permission from Taylor & Francis.

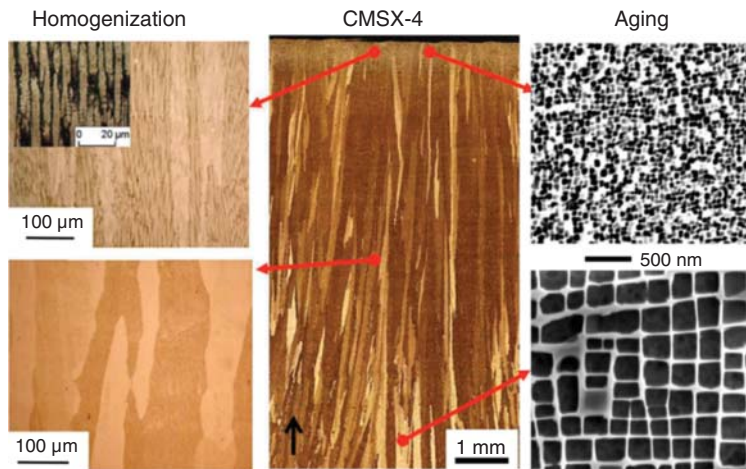


Figure 4.13 Microstructure of a nickel-based alloy CMSX-4 fabricated by EBM with *in situ* heat treatment. Source: Korner (2016)/reproduced with permission from Taylor & Francis.

containing carbides and intermetallic compounds (e.g. FCC γ' -Ni₃ (Al, Ti, Nb) and ordered tetragonal γ' -Ni₃Nb) (Strondl et al. 2008). Note that the columnar γ grains in the matrix have their $\langle 001 \rangle$ orientation parallel to the build direction. Lines of the δ precipitates were present both on grain boundaries and within grains (Figure 4.12c). Such precipitates originated from cellular or dendritic solidification and were mainly formed in highly segregated zones.

Certain non-weldable nickel-based alloys, such as the columnar-grained alloy Rene 142 and the single-crystalline alloy CMSX-4, have also been processed by EBM. In another study by Murr et al., γ' precipitates in printed Rene 142 alloys were found to exhibit an average size of ~ 275 nm with a volume content of $\sim 59\%$ (2013). Figure 4.13 indicates that the dendritic arm spacing of an EBM-printed CMSX-4 alloy was only a few microns. The micro-segregation and homogenization occurring at such a small scale resulted from *in situ* heat treatment, which could also promote the nucleation and growth of precipitates (Ramsperger et al. 2015). Within the alloy, the growth of columnar grains across hundreds of printed layers was also observed (center image). The microstructure of the EBM-printed CMSX-4 alloy was determined to typically include cuboid-shaped γ' -precipitates, which increased with the number of printed layers. Note that aging also occurred during printing because of the long processing time and high temperature.

4.7.3 Cobalt Alloys

Cobalt alloys have been extensively employed in producing valve seats for nuclear power plants, aerospace fuel nozzles and engine vanes, and orthopedic and dental implants because of their excellent mechanical strength at high temperatures, corrosion resistance, wear resistance, and biocompatibility. Figure 4.14 presents the

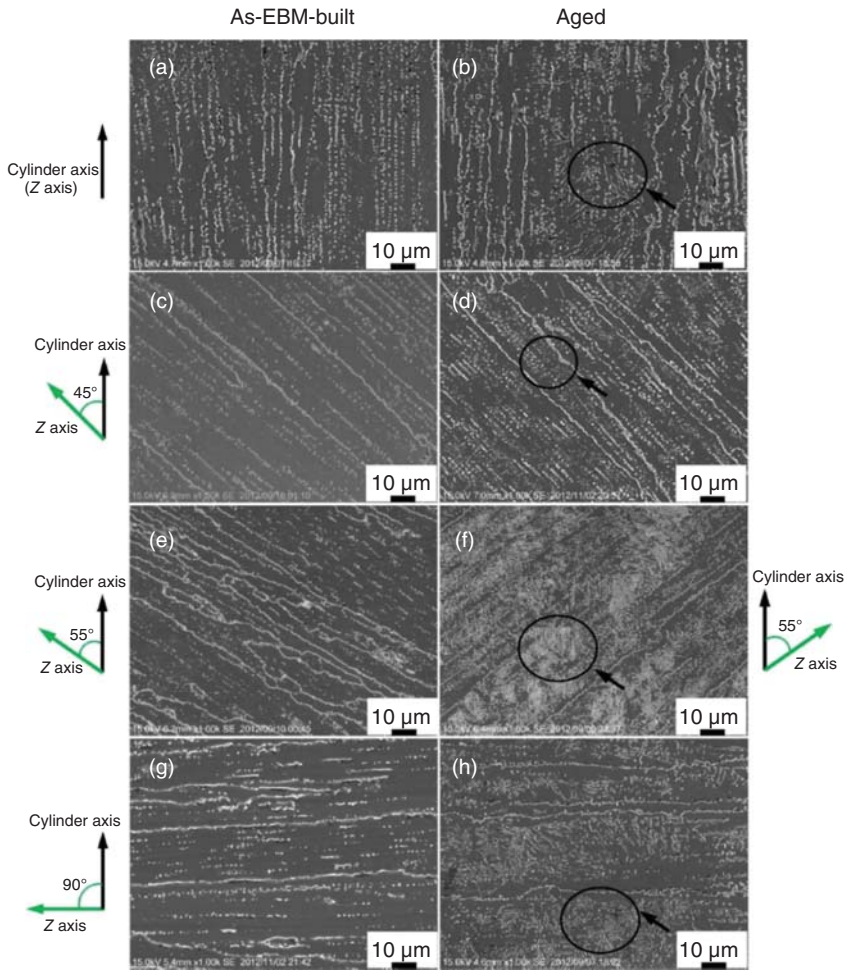


Figure 4.14 Microstructure of an EBM-printed Co–Cr–Mo alloy along the build direction. (a, c, e, g) EBM-printed. (b, d, f, h) Aged at 800 °C for 24 hours. (a, b) 0°-alloy, (c, d) 45°-alloy, (e, f) 55°-alloy, and (g, h) 90°-alloy. The circled regions highlight the dissolution of lamellar precipitates into the matrix. Source: Sun et al. (2014)/reproduced with permission from Elsevier.

microstructures of EBM-printed and age-treated Co–Cr–Mo alloys (Sun et al. 2014). Precipitates aligned along the build direction are observed in the as-built samples. The average distance between the arrays of precipitates was measured to be $\sim 3 \mu\text{m}$. The succedent aging treatment promoted the dissolution of the lamellar precipitates M_{23}C_6 (where M can be Cr, Mo, or Si) into the matrix. It was demonstrated that the precipitates in the lamellar colonies formed after aging were M_2N . The lamellar structures of the M_2N precipitates and the hexagonal close-packed (HCP) ϵ phase were based on the eutectoid transition ($\gamma \rightarrow \epsilon + \text{M}_2\text{N}$).

In Co–Cr–Mo alloys, the γ phase is stable at high temperatures, while the HCP ϵ phase is stable at low temperatures. Therefore, the γ phase may partially transform

into the stable ϵ phase during the printing process. Because of epitaxial growth of the γ phase with a preferred grain orientation in the $\langle 001 \rangle$ direction, the printed parts typically exhibited a pronounced crystallographic texture (Sun et al. 2014). The distribution of the $M_{23}C_6$ precipitates within EBM-printed Co–Cr–Mo products resulted from segregation induced by cellular solidification. After aging at 800 °C for 24 hours, the γ phase was transformed into the ϵ phase, and the grains tended to be equiaxed.

In a study by Tan et al. (2018), an EBM-printed Co–Cr–Mo alloy exhibited fine columnar γ -Co grains with cellular dendrites. Carbide precipitates were formed because of the segregation of carbon into the interdendritic zones and grain boundaries of the alloy. The columnar grains along the building direction in the x - z plane are represented in Figure 4.15a, each of which comprises cellular dendrites with secondary arms. The carbide precipitates at the grain boundaries generated successive thin films that were 100–200 nm thick, thereby separating the columnar grains. The carbide precipitates within the interdendritic zones tended to constitute long chains/clusters along the primary dendrites. At low quantities below 5 vol.%, the carbide precipitates at the grain boundaries and interdendritic zones were difficult to detect via traditional X-ray analysis. Figure 4.15b,c show a representative atom probe tomography (APT) tip sample from the carbide thin film and the APT-reconstructed volume of the four main elements, respectively. The study has determined that Mo-enriched M_xC_y (I) was an M_6C -type carbide, and Cr-enriched M_xC_y (II) was an $M_{23}C_6$ -type carbide.

In general, the mechanical properties of the printed parts exhibit strong anisotropy due to epitaxial solidification. In a study by Xiang et al. (2019), EBM-printed Co–26Cr–6Mo–0.2C samples subjected to a strain rate of 1.67×10^{-4} /s along the horizontal direction succumbed to premature fracture at 334 MPa with an elongation of only 0.23%. In contrast, samples tested along the building direction displayed an ultimate tensile strength of 957 MPa with an elongation of 10.5%. Sun

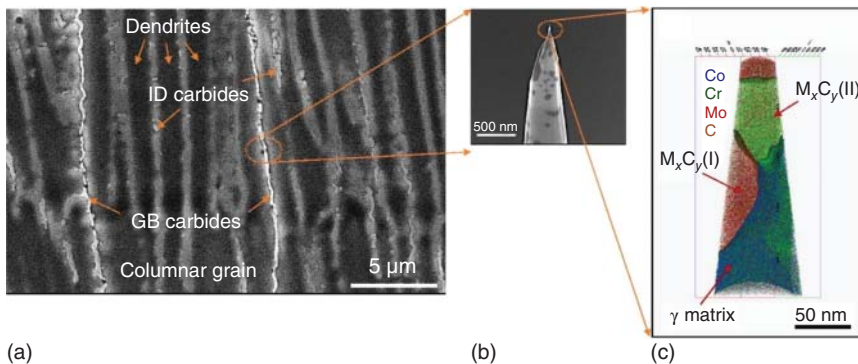


Figure 4.15 (a) SEM image of columnar grains with dendrites in an EBM-printed Co–Cr–Mo alloy. ID carbides: interdendritic carbides. (b) SEM image of an atom probe tomography (APT) tip sample from the carbide thin film in (a). (c) An APT-reconstructed volume featuring two types of carbides and the γ -matrix. Source: Tan et al. (2018)/reproduced with permission from Elsevier.

et al. (2014) demonstrated that at a temperature of 700 °C, a Co–26Cr–6Mo–0.2C sample printed with a deviation of 55° from the z axis possessed the highest ultimate tensile strength of 806 MPa at a strain rate of 1.5×10^{-4} /s.

4.7.4 Iron Alloys

316L stainless steel is a representative iron-based alloy investigated for EBM. Its printability was comprehensively studied by Wang et al. (2018), and the microstructure of EBM-printed 316L stainless steel products was found to exhibit heterogeneity along the building direction, with cellular dendrites and melt pool boundaries present at the top area (Figure 4.16). Few defects were observed at the layer boundaries, which demonstrated that the electron beam was sufficiently strong to fuse neighboring layers (Figure 4.16a). The grains were columnar-shaped and parallel to the building direction because the largest thermal gradient was along the same direction during the printing process. The spacing between adjacent melt pool boundaries was $\sim 100 \mu\text{m}$ (Figure 4.16b), and typical intragranular cellular sub-grains with an average size of $\sim 1 \mu\text{m}$ were obtained (Figure 4.16c).

Figure 4.16d shows the side view of the melt pool and columnar grain boundaries near the top region of the EBM-printed 316L alloy. The columnar grains grew epitaxially across layer boundaries, i.e. epitaxial growth and columnar-shape formation, and their width values were 25–50 μm . They also exhibited a pronounced $\langle 001 \rangle$

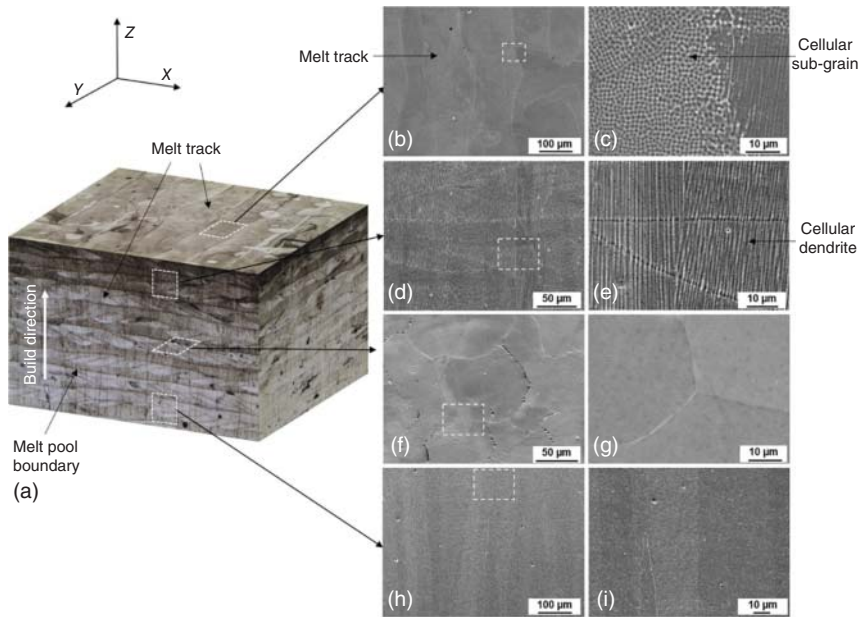


Figure 4.16 Microstructure of an EBM-printed 316L alloy. (a) 3D micrograph under OM; SEM images of (b, c) the x–y plane at the top region, (d, e) the x–z plane at the top region, (f, g) the x–y plane at the middle region, and (h, i) the x–z plane at the bottom region. Source: Wang et al. (2018)/reproduced with permission from Elsevier.

texture, which implies that the alloy possessed anisotropic mechanical properties. Moreover, intragranular dendrites that grew in the same direction as the columnar grains were observed (Figure 4.16e). The average width of the dendrites was $\sim 1 \mu\text{m}$, and cellular sub-grains were identified from their cross-sectional view, which was barely visible below the top region (Figure 4.16f–i). The yield strength, ultimate tensile strength, and elongation of the printed 316L alloy were measured to be in the range of 316–396 MPa, 437–652 MPa, and 9.6–35.2%, respectively. While its strength was higher than its conventional cast and wrought counterparts, it displayed lower elongation. Additionally, the tensile properties of the printed parts along the building direction were superior to those perpendicular to the building direction.

Microstructural analysis of an H13 tool steel printed by EBM indicated that the printed samples lacked macropores and exhibited strong interlayer bonding (Cormier et al. 2004). The hardness of the samples was measured to be 48–50 HRC. The cooling efficiency and dimensional accuracy of an EBM-printed H13 insert with complicated cooling geometries were determined to be higher than those of conventionally cooled core inserts (Rännar et al. 2007).

4.7.5 Others

4.7.5.1 Copper and Its Alloys

Due to their excellent electrical and thermal conductivity, copper and its alloys are promising candidates for applications in electrical and thermal management systems (e.g. heat exchanger devices). However, they are currently unsuitable printing materials for LPBF due to their high thermal conductivity, which results in rapid heat dissipation. Additionally, copper is highly reflective toward lasers, which further hinders the LPBF printing process.

EBM is preferred to LPBF with respect to the processing of copper, as copper possesses different absorption and reflection mechanisms for electrons and photons. In EBM, the amount of energy deposited within the printing material is adequate to consolidate even pure copper (thermal conductivity of 400 W/mK). In addition, copper powder can be rapidly pre-sintered because of its high electrical conductivity. However, the high sintering activity of copper may result in difficulties in removing the powder if it is processed under high pre-sintering temperatures for an excessively long time.

Generally, handling and storing copper is a delicate process as copper is highly susceptible to oxidation. An atomized copper precursor powder with a high Cu_2O concentration was processed by EBM (Ramirez et al. 2011), and copper oxide precipitates were found to contribute to the high hardness and strength of the printed parts. EBM-printed pure Cu parts typically consist of equiaxed precipitate–dislocation cell arrays ($1\text{--}3 \mu\text{m}$) along the building direction, while they comprise elongated or columnar-like arrays with a length of $12\text{--}60 \mu\text{m}$ and corresponding spatial dimensions of $1\text{--}3 \mu\text{m}$ along the transverse directions. In a study that explored directional solidification in EBM-printed parts, a precipitation–dislocation interaction was observed with an increase in their hardness from a base-plate value of 57–88 HV, which is representative of EBM-printed copper products (Guschlbauer et al. 2018).

A process window for dense and crack-free pure copper EBM-printed parts at a building temperature of 530 °C was identified. The EBM-printed copper parts were measured to exhibit a yield strength of 78 MPa, an ultimate tensile strength of 177 MPa, and an elongation to fracture of 59.3%. Cracks in the tensile samples were found to depend on the location of the parts on the substrate and often occur when printed under high-line energy densities.

4.7.5.2 High-Entropy Alloys

EBM has also been adopted to print HEA parts, and the selected HEAs include AlCoCrFeNi, CoCrFeNiTi, and CoCrFeMnNi. EBM-printed AlCoCrFeNi HEA parts have showed the same phase constitutions but distinctive microstructures in the top and bottom zones owing to various temperature distributions caused by preheating and heat transfer (Shiratori et al. 2016). Additionally, dual-phase (B2 + body-centered cubic [BCC]) and FCC precipitates were found within the printed parts. The (Al, Ni)-rich and (Cr, Fe)-rich phases correspond to the B2 and BCC phases, respectively. Preheating at 950 °C led to the precipitation of the FCC phase at the boundaries of the B2 and BCC phases. The decreased temperature gradient within the printed parts also facilitated the BCC-to-FCC phase transformation. Based on a review by Han et al., EBM-printed HEA products could achieve a yield strength of 205–769 MPa, an ultimate tensile strength of 497–1074 MPa, an elongation of 1.2–63%, and a microhardness of 157–500 HV (Han et al. 2020).

Fabricating HEA parts via the *in situ* alloying of at least four premixed pure metal powders through EBM and LPBF remains challenging. In particular, the rapid cooling of melt pools inhibits the convection and diffusion of elements within the metal powders, thereby resulting in the inhomogeneity of element distribution within the printed layers and the anisotropic microstructure of the printed parts.

4.8 Summary

In essence, EBM features the application of a high-energy electron beam to fabricate geometrically complex metal parts in a vacuum environment at an elevated building temperature. This chapter comprehensively covers the historical development, fundamentals, processing, metallurgical defects, powder characteristics, and commercial equipment for EBM, as well as microstructures and mechanical properties of the most extensively studied materials for EBM-printed parts.

A vacuum environment is crucial for processing materials with a high affinity toward oxygen (such as titanium and its alloys). Meanwhile, an elevated building temperature can minimize residual stress and cracking within the printed parts, which is ideal for processing heat-resistant materials prone to cracking (e.g. TiAl). Hence, EBM is a preferred approach for fabricating biomedical implants and aerospace components subjected to stringent requirements. Moreover, the exceptional electron absorptivity of EBM powders enables the processing of materials exhibiting high optical reflectivity (e.g. copper and its alloys).

Compared to LPBF, EBM has disadvantages including low resolution and rough surface of the printed parts, high equipment cost, the requirement for large quantities of printing powder, and significant loss of certain alloying elements. Moreover, EBM-printed parts tend to possess common metallurgical defects such as pores and cracks, although such defects are less pronounced than those in their counterparts printed by LPBF. A major impediment to the widespread adoption of EBM is its small material library, which is partially attributed to the limited number of EBM machine models available worldwide. Existing commercial EBM materials are almost exclusively provided by Arcam, such as Ti-6Al-4V, pure Ti, Co-Cr-Mo, Inconel 718, pure copper, highly alloyed tool steel, and TiAl.

Since generating an electron beam is inherently simpler and less costly than generating a laser beam, the building speed and volume in EBM can be scaled up substantially in the future for ultrafast manufacturing. Future research on EBM should also focus on better process control to obtain higher beam power and quality. With greater precision regarding beam control and the optimization of beam scanning algorithms to prevent “smoking”, finer powders and thinner printing layers can be implemented to print parts with higher resolution and a smoother surface finish.

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5

Laser-Based Directed Energy Deposition

Laser-based directed energy deposition (L-DED) is an additive manufacturing (AM) technique that is fundamentally different from powder bed fusion processes such as laser powder bed fusion (LPBF) and electron beam melting (EBM). L-DED, also commonly known as laser metal deposition (LMD) or laser engineered net shaping (LENS), possesses a unique capability of repairing metal parts. This chapter presents the history, fundamentals, processing characteristics, powder materials, and equipment of L-DED, and it discusses the microstructures and properties of parts printed by L-DED.

5.1 History

L-DED originated from a wire welding technology and was previously known as welding AM (Kratky 1937; Isaac 1942). A patent with early concepts of L-DED was filed in the 1980s, describing a layerwise additive deposition process via laser powder metallurgy (Brown et al. 1982). Subsequently, a method for repairing metal parts through the continuous deposition and melting of powder on their surface was patented (Mehta et al. 1988). In 1988, Hammeke patented a laser spray nozzle, while Buongiorno patented a metal cladding nozzle in 1995 (Hammeke 1988; Buongiorno 1995).

Directed light fabrication was proposed as a form of single-nozzle, powder-based L-DED combining computer-aided design (CAD), computer numerical control (CNC), and laser-based powder deposition for the rapid freeform fabrication of stainless steel parts. In 1995, researchers from Sandia National Laboratories developed a multi-nozzle L-DED system with high powder delivery efficiency, which was commercialized and trademarked as Laser Engineered Net Shaping. In 1997, the Optomec Company also began to promote commercialization of the technology.

Different L-DED techniques have emerged in the past 20 years with varying degrees of success in terms of commercialization and market/research adoption. A wide range of terminologies has been proposed for L-DED, including LMD, LENS, direct metal deposition (DMD), and laser rapid forming. A new generation of the L-DED technology is currently being developed by several companies under the generic name of laser metal deposition.

5.2 Fundamentals

In L-DED, metal powder and/or wires are directly deposited onto a freeform substrate in a layer-by-layer manner while being melted by a laser beam. A schematic of the L-DED process is shown in Figure 5.1a. The printing head consists of a focused laser source and a powder delivery system in the form of a coaxial, multi-stream, or side nozzle. The laser beam creates a melt pool on a substrate or a pre-deposited layer, which moves along a predefined scanning path. The powder is delivered from powder hoppers through the nozzle by a carrier gas, which is usually argon or helium, and injected into the melt pool, which subsequently cools and solidifies once the laser beam moves away. The created melt pool displays different penetration depths depending on the process parameters (Figure 5.1b). After the deposition of a layer, the print head moves away from the solidified surface by a preset distance before the next layer is deposited.

The aforementioned process is repeated until the entire part is fabricated. Generally, it is desired to use a substrate with a similar chemical composition to the printed material. Due to the comparable thermal properties and suppressed brittle intermetallic phases between the printed materials and the substrate, decent interfacial bonding can be achieved between the first deposited layer and the substrate to avoid delamination.

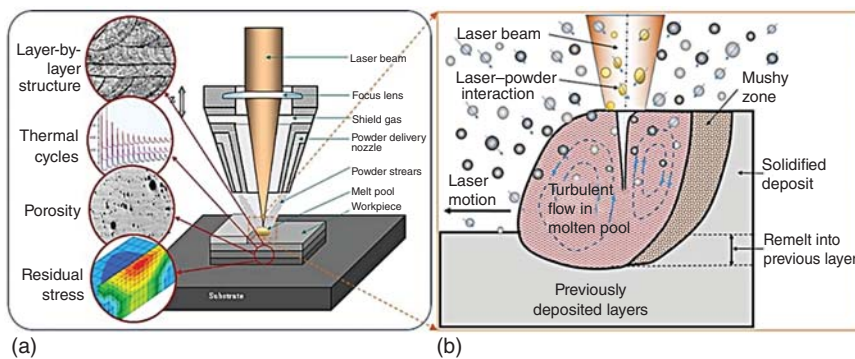


Figure 5.1 Schematic diagrams illustrating the attributes and mechanisms pertaining to L-DED. (a) Microstructure, multiple interfaces, thermal cycles, defects, and residual stress, and (b) interactions among the injected powder, laser beam, and melt pool. Source: Reproduced from Zheng et al., (2019)/with permission of Elsevier.

The advantages of the L-DED process are as follows:

- An L-DED machine can be equipped with multiple powder feeders. Multiple powders can be delivered and printed simultaneously, which enables the fabrication of multi-materials such as functionally graded materials.
- The simultaneous delivery of different powders allows for *in situ* alloying, which can achieve high-throughput screening of the composition of newly developed metal materials.
- The deposition head is installed on a four- or five-axis motion system, which enables printing on a curved surface. L-DED is thus suitable for repairing damaged parts and adding new features to existing parts.
- The L-DED process corresponds to a high building rate, which is favorable for printing relatively large parts.
- L-DED additive and subtractive manufacturing can be simultaneously conducted by sharing the motion control system to improve the dimensional accuracy and surface quality of the printed parts.

The L-DED process presents the following disadvantages:

- Large temperature gradients may induce residual stress within the printed parts, resulting in deformation and cracking.
- Low printing resolution of the machines resulting from large melt pools leads to the printed parts undergoing shape deviation and exhibiting rough surfaces. Thus, post-machining procedures are required to improve the dimensional accuracy and surface quality of the printed parts.
- The design freedom and geometrical complexity pertaining to the parts are limited, particularly for L-DED machines confined to three degrees of freedom.
- The efficiency of powder usage and powder recyclability is low.

The main process parameters of the L-DED process include the laser power, laser spot diameter, scanning speed, powder flow rate, scanning strategy, hatch spacing, and dwell time between each deposited layer. The optimal process parameters depend on both material properties (e.g. laser absorptivity and powder flowability) and machine configurations (e.g. types of nozzles and powder feeders).

The powder particles absorb a fraction of the laser energy during the printing process. The remaining energy is delivered to the substrate to form a melt pool or dissipated through reflection or refraction. The amount of energy absorbed by the powder is determined by the type of laser beam and the powder material, as discussed in Section 3.2.

The amount of energy absorbed by the powder also depends on its flow rate, the size of its particles, and the nozzle geometry. A high powder flow rate or a large particle size results in the melting of more powder particles (Wolff et al. 2020). Single feed nozzles (or side nozzles) installed on one side of the laser beam can result in asymmetric energy absorption and formation of thermal gradients, leading to dimensional inaccuracy and inhomogeneity within the microstructure of the DED-printed parts. Instead, coaxial nozzles are preferred to tackle this issue due to the uniform deposition of powder surrounding the energy source (Svetlizky et al. 2021).

Since mainstream engineering metal materials (e.g. iron-, nickel-, and titanium-based alloys) are highly absorptive with respect to neodymium-doped yttrium aluminum garnet (Nd:YAG), CO₂, and fiber lasers, these three types of lasers are commonly employed in commercial L-DED equipment. Their usage and limitations are discussed in Section 3.2. The laser power determines the amount of energy delivered to the deposited powder and the substrate (see Eq. (5.1) in the subsequent Section 5.3). A high laser power results in a large melt pool and deep penetration into the preceding solidified layers. However, a high laser power can induce spattering of molten droplets and vaporization of alloying elements from the melt pool, which may damage the nozzles and degrade the mechanical properties and surface roughness of the printed parts. In contrast, lower laser power can lead to the formation of defects, such as lack-of-fusion pores and incomplete melting of powders.

The powder flow rate can affect the surface roughness and grain texture of L-DED-printed parts. An increase in the powder flow rate can lead to increased surface roughness, which is attributed to insufficient energy to fully melt the powder particles, resulting in partially melted particles being embedded into the surface of the printed parts (Chen et al. 2021). Additionally, a high powder flow rate can influence the grain texture as it affects the thermal gradient of the melt pool, resulting in equiaxed grains instead of the columnar grain texture commonly observed in AM-printed parts (Zhang et al. 2021). Conversely, a low powder flow rate can lead to insufficient material being deposited onto the preceding layers.

The scanning speed influences the material deposition rate, as well as the melting and solidification rates. A high scanning speed results in a small amount of powder being deposited and a short laser interaction time, and thus a small melt pool is formed (Chen et al. 2021). On the other hand, a continuous increase in the scanning speed can result in hydrodynamic instability of the melt pool, leading to the poor surface quality of the printed parts (Svetlizky et al. 2021).

Scanning strategies for the L-DED process, such as unidirectional and bidirectional scanning with 0° or 90° rotation vectors, spiral patterns, and fractal patterns, are commonly employed in L-DED (Svetlizky et al. 2021). As discussed in Section 3.2, the scanning pattern determines the amount of residual stress within the printed parts and affects their mechanical properties. Additionally, the dwell time between each deposited layer can be tailored to take advantage of the repetitive heating and cooling cycles of L-DED to trigger precipitation hardening, control the microstructure, and reduce residual stress (Amirabdollahian et al. 2021; Guévenoux et al. 2020; Denlinger et al. 2015).

To optimize the printing process, interactions between the various process parameters must be considered because they affect the relative density, surface roughness, microstructure, defects, and mechanical properties of the printed parts. Experimental tools such as the design of experiments (DOEs) can be applied to determine the optimal processing parameters. DOE allows the user to identify the interactions between various process parameters and establish the relationships between these variables and the resultant microstructure, mechanical properties, and surface

finish of the printed parts. For instance, the energy density of the laser beam is synergistically dependent on the laser power (100–5000 W), laser spot diameter (up to 4 mm), scanning speed (1–30 mm/s), and powder flow rate (10–100 g/min). Meanwhile, the scanning pattern, hatch spacing, and interlayer cooling time collectively affect the thermal distribution and history of the melt pools. Notably, the cooling rates of L-DED systems typically range between 10^2 and 10^4 K/s (Zheng et al. 2008). The focal plane of the powder flow usually coincides with the substrate, on which the laser beam can be focused or defocused. Scanning configurations, such as raster, offset-out, spiral, and fractal deposition patterns, which dictate the tool path of the printing head, are implemented before the printing process.

5.3 Deposition Process

The deposition process of L-DED comprises energy flow (laser), feedstock flow (metal powder), gas flow (carrier gas and shielding gas), and information flow (numerical control and *in situ* monitoring). Several interconnected physical phenomena occur within a short time span during the process: (i) laser/powder/gas interactions; (ii) initiation, stabilization, and solidification of the melt pool; (iii) thermal transfer activities (i.e. thermal convection in melt pools, thermal conduction from the melt pool to printed layers, substrates, and the atmosphere, and thermal cycling) induced by the layer-wise printing process.

Laser/powder/gas interactions are highly transient and depend on the laser properties (e.g. power, wavelength, and energy profile), powder properties (e.g. energy absorption rate, morphology, and particle size distribution), and atmospheric conditions (e.g. gas type and flow rate). The formation of plasma (i.e. ionized gas), the fourth state of matter, can be induced by the vaporization and ionization of in-flight powder by a high-power laser. The presence of plasma between the powder particles can significantly affect their energy absorption and lower the printing efficiency. Additionally, such plasma can contribute to nonlinear positive pressure effects that restrict the amount of vapor escaping the melt pool, thereby increasing the porosity of the printed parts. Such degradation can be avoided by implementing a proper combination of laser power and powder flow rate to prevent the in-flight powder from overheating. Plasma effects can be further suppressed by employing shielding gases (such as helium and argon) in the L-DED system. The term “specific energy” quantifies energy delivery, which is described in terms of the area energy density E as

$$E = \frac{P}{2r_b V}, \quad (5.1)$$

where P is the laser power, r_b is the laser beam radius, and V is the scanning speed.

The laser/powder interaction (or exposure) time t can be estimated by $t = 2r_b/V$, and t typically varies from 0.2 to 8 ms (Simchi 2006). When in-flight powder ejected from the nozzle is exposed to the laser beam, it undergoes steep heating from the laser beam. Excessive energy input by the laser beam can lead to element loss from the powder in the form of evaporation (Kruth et al. 2004). The in-flight powder particles are primarily cooled by the surrounding carrier gas and shielding gas through

thermal convection. Such gases can impede the momentum of the powder particles by applying a drag force on the material jet stream, which decelerates and destabilizes the powder particles during their flight.

The laser beam creates a melt pool on the substrate, and a molten metal stream is injected into the pool, whose dimensions depend on the process parameters. Only a portion of the incident laser energy is absorbed by the powder to initiate and maintain the melt pool, while the rest is lost through reflection. The absorbed energy is dissipated via radiation, convection (shielding/carrier gas), and conduction (substrate and printed layers).

Radiation heat transfer during deposition is governed by the spectral emissivity of the melt pool, which is a function of its superheating temperature and the oxygen concentration within and around it. Therefore, the dimensions and temperature profile of the melt pool are also sensitive to changes in its emissivity (Wang and Felicelli 2006).

In addition, the temperature field and morphology of a melt pool are determined by interfacial forces such as the surface tension and recoil pressure of the metal vapor, which are more prevalent at its surface and beneath its center, respectively. As a result, the highest superheating temperature of a melt pool is obtained at its surface center, which is sufficient to vaporize the molten metal. Consequently, metal vaporization occurs at the surface of the melt pool, resulting in keyhole formation. Once the keyholes collapse, and the melt pool solidifies, ambient gases are trapped within the latter, and pores are formed due to its high solidification rate.

As the temperature of the melt pool rises, the recoil forces within it increase more rapidly than its surface tension. When the vapor recoil force exceeds the liquid–gas surface tension force near the periphery of the melt pool, the liquid within the melt pool is ejected. An increase in bulk temperature near the melt pool can cause it to boil and result in a loss of mass. The tendency for liquid metal ejection to occur as a result of vapor recoil forces increases, and the vapor recoil force F_r can be estimated by

$$F_r = \int_0^{r_m} r \Delta P(r) dr, \quad (5.2)$$

where r_m is the radial distance at which the melt pool surface reaches its boiling point, and $\Delta P(r)$ is the difference between the local equilibrium vapor pressure and the atmospheric pressure (He et al. 2005). Heat loss due to vaporization of the melt pool can be detrimental to the quality of L-DED products.

During L-DED, substantial variations in the temperature field of the melt pool result in steep density and surface tension gradients along its length and depth, producing free convective and Marangoni-type flows, respectively. Diffusive motion related to turbulence can significantly affect the solute and momentum transport within the melt pool and enhance convective heat transfer. As the melt pool becomes deeper (i.e. penetration depth increases), its vorticity increases, which indicates higher turbulence.

When the surface tension gradient of the melt pool is small, evaporation heat loss becomes non-negligible, and the peak temperature of the melt pool is lowered.

Conversely, a large melt pool surface tension gradient reduces the influence of vaporization heat loss on the peak temperature and shape of the melt pool. In particular, a negative melt pool surface tension/temperature gradient leads to an outward flow toward the periphery of the melt pool, rendering it wide and shallow. In contrast, a positive surface tension/temperature gradient induces a narrow and thick melt pool due to inward flow toward its center. The presence of a mushy zone near the liquid–solid interface at the solidification front also influences the dynamics of the melt pool.

The powder flow rate and angle of attack of the powder particles significantly affect the free surface stability and motion of a melt pool. Meanwhile, small powder particle sizes result in a stable melt pool for L-DED. In contrast, large powder particles can produce a highly agitated and unstable melt pool, corresponding to free surface instability. The agitating motion of an unstable melt pool is attributed to the relatively high momentum inherent in large powder particles, resulting in large displacements within it and oscillations along its free surface.

As the number of deposited layers increases, heat accumulation leads to a higher temperature within the previously deposited layer, and the cooling rate of the melt pool decreases. Thus, more powder particles can be deposited onto the preceding solidified layer, leading to a higher layer thickness. High powder feed rates can also result in the powder particles splashing, which affects the surface quality of the printed parts and damages the deposition head and protective lens.

The dimensions of a melt pool are collectively determined by multiple process parameters, including the laser power, scanning speed, laser spot diameter, and powder flow rate (Figure 5.2). The preheating temperature of the substrate (or previously deposited layers) and interlayer cooling time may also influence the melt pool dimensions (Figure 5.2b) because they affect the energy absorption and temperature distribution of the melt pool by controlling its thermal history. The melt pool width and temperature generally increase with the laser power and decrease with the scanning speed, both of which influence the cooling rate at the liquid–solid interface. As shown in Figure 5.2a, the melt pool dimensions (width and depth) increase almost linearly with the laser power and incident energy density (Zheng et al. 2019).

As the laser power increases, the width of the melt pool increases more rapidly than its depth, indicating that the former is more susceptible to changes in laser power than the latter. If the powder flow rate is preset, the amount of powder delivered and deposited per unit time is almost fixed. For a constant hatch spacing (defined in Chapter 3), the melt pool width and height increase with the laser power, while the layer thickness increases with the powder flow rate and decreases with the scanning speed, as shown in Figure 5.2a,c.

The melt pool width can also be adjusted by altering the laser spot diameter, which determines the area exposed to laser irradiation on a deposited layer. A decrease in the laser spot diameter at a constant laser power increases the energy density of the laser beam, which causes a decrease in the melt pool width and leads to a large contact angle of a single track if excessive powder particles are present. A large contact angle is undesirable as it may induce porosity in the overlapping regions between adjacent tracks.

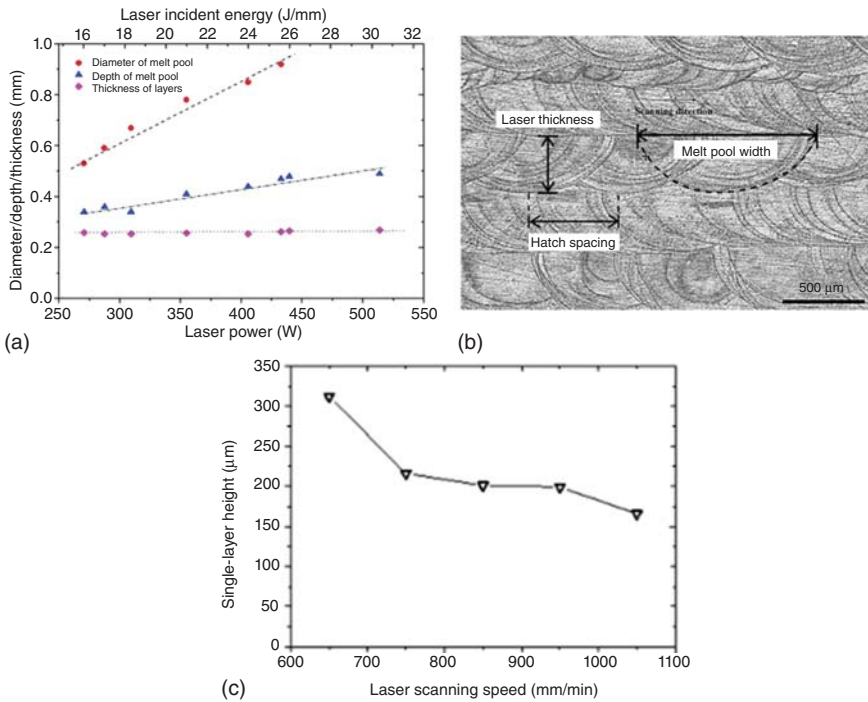


Figure 5.2 (a) Variation in the melt pool size and deposited layer thickness of 316L printed by L-DED with respect to laser power and laser incident energy (laser power/scanning speed). (b) OM image of the typical morphology of a melt pool, which comprises etched patterns. Source: Zheng et al. (2019)/reproduced with permission from Elsevier. (c) Variation in the layer thickness of AISI M4 printed by L-DED with respect to the scanning speed. Source: Reproduced from Shim et al. (2016)/with permission from Elsevier.

A narrow melt pool may collapse before solidifying when the powder is deposited onto an inclined surface. This effect is attributed to a decrease in its cooling rate from excessive heat input. Such collapse may also result from a high powder flow rate and sufficient energy input providing an abundant supply of melt stream, which is injected into the melt pool and pushed outward. Thus, a deposited track with a width greater than the laser spot diameter can be formed.

The free surface of a melt pool governs the cross-sectional profile of a deposited layer. Consequently, the resultant liquid–vapor interface (i.e. melt pool–vapor gas mixture interface) is unstable and in non-equilibrium. Meanwhile, the movement of the laser beam and powder injection results in a slanted melt pool profile (Figure 5.1b). The angle of such inclination is related to the deposition layer thickness and melt pool morphology.

For multi-track deposition, the morphology of a melt pool becomes more asymmetric and slanted because of the overlap of adjacent tracks. For secondary adjacent track deposition, the melt pool is inclined toward the previously deposited track, thereby altering heat transfer and the melt pool wetting behavior. Multi-track deposition is also susceptible to the remelting of adjacent tracks and preceding

layers. Moreover, the type of nozzle utilized (coaxial nozzle, multi-stream nozzle, etc.) and the nozzle configuration (lateral injection nozzle, radially symmetric injection nozzle, etc.) affect the morphology of the melt pool by changing its tilt angle.

The solidification of a melt pool is governed by its net heat transfer; it can be classified into three major events: heterogeneous nucleation, mushy-zone heat/mass transfer, and microstructural evolution via intrinsic heat treatment.

The mushy zone contains a two-phase mixture of remnant molten metal and solid particulates; it can be identified as the region between the melt pool and the solidified material, as shown in Figure 5.1b. Natural convection is the primary mode of heat transfer in the mushy zone, as significant density variation exists within it. The mushy zone is a result of melting and solidification occurring between the solidus and liquidus temperatures, as observed by the coexistence of liquid and solid metals.

The heat transfer at the liquid–solid boundary of the melt pool is perhaps the most complex physical process inherent to powder-based L-DED. The increase in mass of blown powder disturbs the transient morphology of the melt pool and contributes to its instability; the trailing edge of the melt pool releases its latent heat of solidification, which further increases the complexity of the process. As a result, the cooling rate is the highest at the liquid–solid interface and decreases closer to the center of the melt pool.

The powder particle momentum can be transferred with minimal momentum loss when impacting the surface of the mushy region, as the powder particles do not rebound or melt, which induces shear stress toward the leading edge of the melt pool. The trailing edge undergoes turbulent flow and a drastic shape change due to the competition between the forward shear stress and upward surface stress induced by Marangoni flow, resulting in disturbance to the temperature distribution during melting. Such disruption of the surface flow and temperature distribution may impede the continuous epitaxial growth of the crystals during rapid solidification.

The initial temperature of the substrate significantly influences the microstructure of the region of a printed part near it because the thermal gradients of the first few deposited layers are determined by the temperature of the substrate and the melt pool. Preheating the substrate reduces residual stress within the printed parts and lowers the risk of cracking and/or thermal distortion. In some cases, partial remelting of the substrate is performed to ensure firm bonding between the substrate and printed part, in addition to the uniformity of the microstructure at their interface.

5.4 Metallurgical Defects

Common metallurgical defects in L-DED parts include porosity, high surface roughness, and cracks. The mechanisms of pore formation in L-DED are similar to those in LPBF, which can be attributed to insufficient melting, entrapped gas, and debris. Lack-of-fusion pores are usually formed in the overlapping region of adjacent tracks when a mismatch between the melt pool size and the hatch spacing exists. The insufficient supply of molten material prevents the gaps between the adjacent tracks from being filled when subsequent layers are printed under low laser powers,

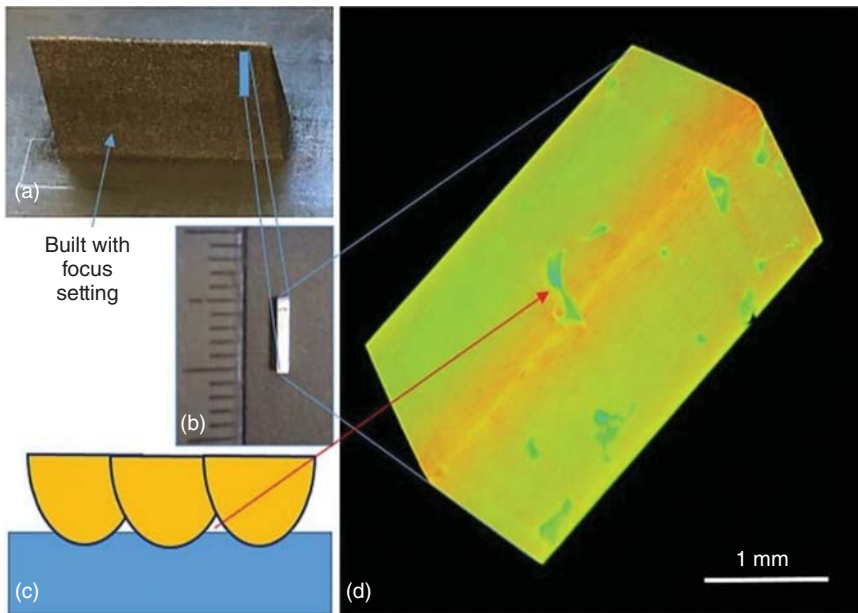


Figure 5.3 Porosity in a 316L sample printed by L-DED measured with X-ray computer tomography (X-CT). (a) Photo of the sample, (b) testing sample removed from the printed sample for X-CT measurement, (c) schematic diagram for the formation of lack-of-fusion pores, and (d) 3D X-CT measured results. Source: Zheng et al. (2019)/reproduced with permission from Elsevier.

high scanning speeds, or high powder feed rates. This phenomenon is particularly prominent during the initial deposition process because this region possesses a higher cooling rate than the other regions. These pores exhibit irregular shapes with coarse inwalls, as presented in Figure 5.3. Lack-of-fusion porosity is rarely observed and can be easily avoided with the proper selection of process parameters.

Gas pores usually exhibit spherical shapes with smooth inwalls. They are randomly distributed within the parts and are either generated through gas entrapment during melting and solidification or by gaseous impurities in the feedstock powder (Wang et al. 2014). The gas porosity in deposits is generally less than 0.5% per unit area.

Porosity arising from unmelted powder particles is most likely present in the initial deposition layers, in which a large amount of heat is expended to initiate the formation of the melt pool and is transferred to the substrate at the beginning of the L-DED process. The effectiveness of increasing the laser power to reduce porosity is limited by the formation of spatters, which reduce the surface quality of the printed part. Meanwhile, higher laser power increases the risk of keyhole pore formation. Porosity can also result from turbulent fluid flow, which occurs due to the quick collapse of keyholes and rapid solidification of the melt pool that prevents keyholes from being filled. As a result, keyhole pores primarily appear at the bottom of the melt pool, and this phenomenon is the leading cause of micro-porosity.

In general, porosity can be reduced to a certain extent by optimizing the process parameters, such as implementing a proper combination of the laser power and scanning speed to control the melt pool temperature and cooling rate during L-DED. The laser power, scanning speed, powder flow rate, and hatch spacing are a few of the most important factors in controlling the porosity level.

The poor surface finish of L-DED parts can be attributed to a large melt pool size, spatters attached to the melt track surface, partially melted powder, and the layer-by-layer nature of the fabrication process. Surface roughness values between R_a of 4–200 μm have been reported for L-DED-printed Ti–6Al–4V parts, while they vary between R_a of 5–10 μm in LPBF-printed Ti–6Al–4V parts (Ahsan et al. 2011). The deposited layers and melt pool boundaries are visible to the naked eye during the deposition process. The surface roughness of L-DED parts can be controlled by process parameters, powder size and morphology, focal distance, laser profile, and laser-powder alignment. For instance, the surface roughness tends to increase with the powder flow rate and the use of powder obtained from the gas atomization process instead of the plasma rotating electrode process.

The degradation of the side surface quality caused by the excessive accumulation of adherent powder particles is shown in Figure 5.4a. The agglomeration of unmelted powder adhering to the side walls of deposited components is related to two types of misalignment: misalignment of the laser beam relative to the focus lens and misalignment of the focused laser beam with respect to the focused powder stream.

Misalignment of the laser beam with the focus lens may cause one side of the component to receive excessive laser power input and vice versa (Figure 5.4d), leading to the accumulation of powder particles on the side surfaces of the printed parts, as indicated by the red arrows in Figure 5.4a.

The misalignment of the laser beam with the powder stream can also result in some of the injected powder particles attaching to the side surface of the builds due to the non-equilibrium kinetic energy and inhomogeneous distribution of injected powder passing through the laser beam region (Figure 5.4e). To prevent this misalignment, the optical system was modified in a study to permit a variable focal distance, which allowed the laser focal plane to be positioned above or below the surface of the workpiece (positive or negative defocusing conditions). The implementation of identical parameters with an adjustable laser focal plane significantly improved the surface quality, as shown in Figure 5.4b.

The unmelted or partially melted powder can also attach to the top surface of a part produced by L-DED. Figure 5.4c displays a contour map detailing the topography of the top surface. The results reveal that the top surface comprised alternating layered ridges originating from the multi-pass deposition process. The top surface also contained unmelted or partially melted powder particles. As the laser spot moved away from the melt pool, the decreasing temperature of the melt pool was insufficient to fully melt the powder particles, causing them to fuse with the cooled-down surface. Some unmelted or partially melted powder particles were delivered to the solidified tracks due to defocused powder delivery or spattering. These powder particles were spatially concentrated along the metal flow trajectories and/or inter-pass boundaries.

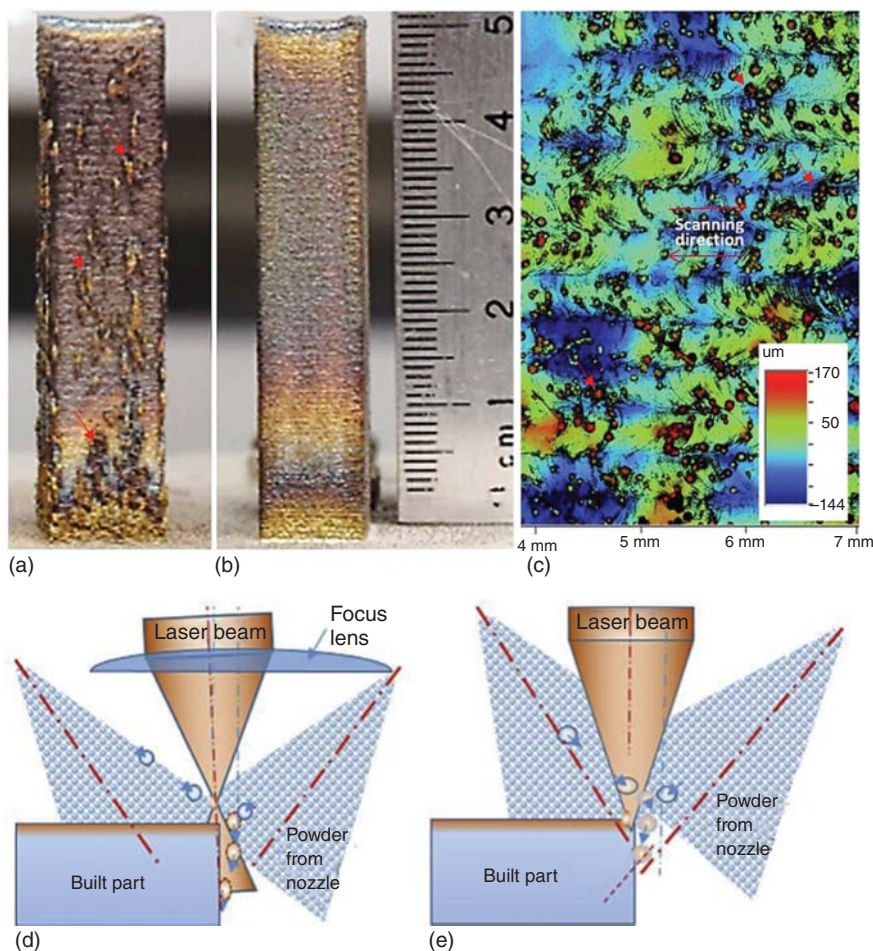


Figure 5.4 Surface quality of 316L samples printed by L-DED. (a) Side surface with adherent powder particles obtained with the laser set to an over-focused condition; (b) side surface without adherent powder particles obtained with an under-focused laser; (c) top layer surface topography illustrated by a contour map with a profilometer, showing unmelted or partially melted powder particles. Schematic diagrams indicating the misalignment of the laser beam with the (d) focus lens and (e) powder feeder. Source: Zheng et al. (2019)/reproduced with permission from Elsevier.

5.5 Powder Materials

The powder properties adopted in L-DED are similar to those in PBF processes, except L-DED employs a wider powder particle size distribution ranging from 50 μm to 150 μm . Gas atomization, water atomization, and plasma rotating electrode processes are typical methods of producing printable powder for L-DED. Therefore, the shape, surface quality, porosity, flowability, purity, and size distribution of the produced powder should be evaluated before usage. L-DED can print a broad spectrum

Table 5.1 Summary of powder materials for L-DED, including commercialized materials and laboratory materials.

Material	Commercial equivalents
Titanium	Commercially pure Ti, Ti–6Al–4V, Ti6242, TC21, TA15
Steel and iron	316L, 304, 254SMO, 2205, 431, 17-4 PH, S53, maraging steels, Hadfield steels, P20, M4, H13, CPM 10V, X42Cr13, Invar steels, G3Si1,4130, 4140, 300M
Aluminum	AlSi5, Al–Si10–Mg, AlSi12, Al–Si–7Mg, AlMgScZr
Nickel	Inconel 718, Inconel 625, Hastelloy, Monel, CMSX-4, René, high-Cr NiCr
Cobalt	Co–Cr–Mo
Copper	CuAl, CuNi, CuAlNi, CuSn, CuSi3, CuCrZr
Tantalum	Pure Ta
Molybdenum	Pure Mo
Magnesium	Magnesium alloys
Tungsten	Pure W

of materials, including iron-, titanium-, aluminum-, nickel-, cobalt-, copper-based alloys, and their composites, which are widely employed in various industrial applications. A summary of printable materials for L-DED is listed in Table 5.1.

L-DED can be equipped with multiple powder feeders, which render it capable of printing multi-materials, hierarchical materials, and functionally graded materials. It can also potentially improve the performance of high-entropy alloy products by increasing the complexity and functionality at user-definable locations. Furthermore, compared to PBF, L-DED is compatible with pre-alloyed high-entropy alloy (HEA) powders and pure elemental powders delivered from multiple powder hoppers simultaneously to print HEA products through *in situ* alloying (Han et al. 2020). This ability eliminates the requirement for a powder preparation process, which incurs a long lead time and high cost. Meanwhile, the flexibility of the composition design of HEAs for materials development is also enhanced.

5.6 Equipment

L-DED simultaneously delivers powder materials and energy, which is accomplished through the controllable integration of powder and energy delivery systems. A typical L-DED machine consists of a laser system, a powder feed system, a motion control system, and auxiliary systems such as monitoring and environmental control systems, as shown in Figure 5.5.

Most L-DED machines employ continuous-wave lasers of infrared wavelength. Some machines allow for an adjustable laser spot diameter, focal length, and laser energy profile that provide versatility during the printing process. The laser beam

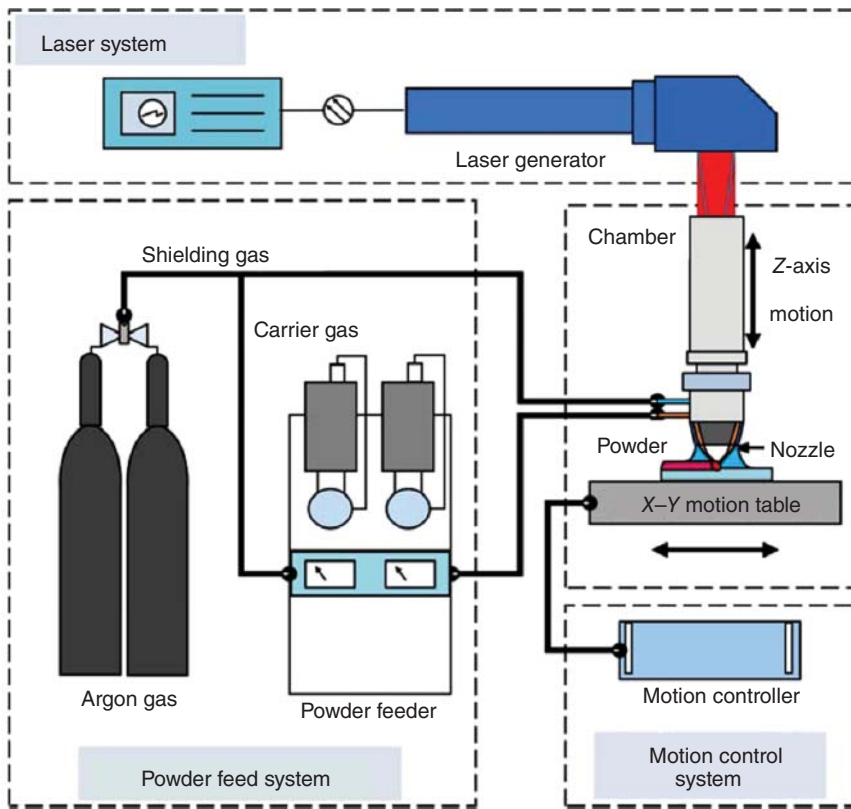


Figure 5.5 System components of an L-DED machine. Source: Kim et al. (2017)/MDPI/CC BY-4.0.

travels through the optical fiber in the printing head and is focused on the deposition region through a planoconvex lens.

For most systems, Nd:YAG and fiber lasers typically exhibit a laser power range of 1–5 kW. However, other types of lasers, such as CO₂ and pulsed-wave lasers, can be employed if sufficient power is available for melting the material. The Nd:YAG laser has been widely applied in many laser-based processing applications, including laser welding, cutting, and coating, since most metals exhibit poor reflectivity toward its incident spectral radiation at a wavelength of ~ 1067 nm. CO₂-type lasers possess wavelengths of an order of magnitude higher at 10.6 μm and may contribute to a less energy-efficient L-DED process.

In general, the diameter of the laser beam is typically a few millimeters, and the energy intensity of a continuous-wave laser displays a near-Gaussian distribution. Extreme heat fluxes are also present within the melt pool. For example, an L-DED process operating with a laser power of 500 W and a laser spot size of 1 mm produces an average heat flux of over 63.6 kW/cm².

Laser attenuation occurs due to the absorption and scattering of laser radiation by the blown powder. The powder stream profile affects both the radial laser power

intensity profile and the ratio of the attenuated laser power to the original laser power. For a fixed laser power, increasing the powder flow rate results in a decrease in the mean temperature of the powder stream and a higher degree of laser attenuation for a Gaussian irradiation profile. The effects of laser attenuation can be significant and result in only 75% of the original laser power reaching the melt pool surface (He and Mazumder 2007). To mitigate such an issue, a coherent beam of a wavelength easily absorbed by the powder is desired.

Since the laser optical system and powder feed nozzles are designed to focus on a specific location, a precise stand-off distance must be predefined for optimal deposition. Changes in the focal distance to the substrate caused by misalignment, overbuilding, or in-process distortion can result in variations in the powder feed and laser focus alignment, which may adversely affect the printing process.

The powder delivery performance of the L-DED process can be evaluated by the powder flow rate, which is the mass of powder delivered per unit time. Meanwhile, the powder utilization efficiency can be assessed by the mass ratio of the deposited powder to the delivered powder over a specific time interval. Additionally, the powder utilization efficiency depends on the nozzle geometry, powder delivery angle, laser and powder flow process parameters, and flowability and size distribution of the powder particles. A low deposition efficiency typically corresponds to a low building rate and a significant amount of recycled and/or “scrapped” metallic powder. As a result, the manufacturing cost and complexity associated with the routine cleaning/recycling procedures regarding the L-DED process increase.

As shown in Figure 5.5, the powder delivery system primarily consists of powder dispensing components (i.e. pipes and carrier gases), a printing nozzle (in coaxial, multi-stream, or side nozzle form), and auxiliary components (e.g. mass and gas flow sensors). Metal powder is dispensed from a hopper/container into a connected feeding line, in which it is carried by an inert gas such as argon or helium. The powder stream delivered to work sites may fluctuate at a low frequency, and such irregularities can be detected and rectified by a monitoring system. Notably, the nozzles are specially designed and positioned to ensure that the material stream intersects with the laser beam and is injected into the melt pool.

The angle of attack and spatiotemporal uniformity of the powder jet can be achieved through the proper design of the powder feeding system. The shape of the powder stream, speed of the blown powder, laser intensity distribution, and blown powder temperature distribution are all significantly affected by the feeding angle with respect to the nozzle and the imposed powder feeding rate. However, the deposition uniformity of the powder is nearly independent of the relative laser/substrate speed. The number of coaxially blown powder particles per unit volume, or powder volume concentration, can be modeled by

$$N(r, l) = N_{\max}(l)e^{-2r^2/r_p^2}, \quad (5.3)$$

where r is the distance from the beam centerline, l is the laser/powder working distance, $N_{\max}$ is the maximum volume concentration, and r_p is the characteristic powder stream radius (Peyre et al. 2008).

Compared to coaxial nozzle and multi-stream nozzle L-DED systems, maintaining flow uniformity and printing functional multi-materials present a challenge for a side nozzle system. However, for parts with complex geometries, coaxial nozzles and multi-stream nozzles provide relatively high powder deposition efficiency, in which the powder particle stream diameter matches the laser beam diameter.

Since metals exhibit relatively high melting temperatures, the printed parts are highly prone to oxidization during L-DED. Therefore, inert shielding gases such as argon are utilized to protect the deposition area by displacing the oxygen within the printing chamber and powder delivery system to create an inert atmosphere. While oxygen tolerance in L-DED varies with applications and materials, oxygen concentration levels below 10 ppm are typically acceptable in a controlled atmosphere. The chamber is purged at a shielding gas flow rate of 5–20 L/min, with the carrier gas purge rate being governed by the powder feed rate.

Monitoring and control systems are required to ensure a stable laser power output, precise and accurate movement of the printing head and substrate stage, a well-defined material feed rate, and constant chamber pressure and gas concentrations during processing. Monitoring systems capable of detecting scattered or reflected light, such as light waves reflected by turning mirrors or have undergone Rayleigh scattering in the air, exhibit potential for nonintrusive, real-time measurements and assessments of both internal and external laser beam power fluctuations. The laser reflected from the melt pool to the protective glass can be detected by a photodiode, which protects the optical components from being damaged by the reflected laser beams when processing highly reflective materials.

To ensure part quality, a trace oxygen sensor typically monitors the oxygen concentration within the build environment. Electrochemical oxygen sensors can measure concentration on the scale of parts per million, but they require periodic calibration.

In powder delivery systems, real-time monitoring and control of the flow rate can be achieved through continuous weight measurement, camera imaging, and laser diffraction methods. However, due to dull mass flow responses, long delivery routines, and slow sampling rates, a significant delay exists between the changing and stable outputs of the powder flow. Furthermore, controlling the powder flow rate precisely and quickly during the process is challenging.

The selection of process-dependent build attributes requires prior knowledge of the desired part geometry, material composition, density, microstructure, etc. Many characteristics, such as material composition, density, and microstructure, cannot be directly measured. However, certain characteristics of the laser-material interaction and solidified regions of the deposit can be detected to allow for estimations and indirect monitoring of these variables. By coupling imaging systems with a laser deposition system, the melt pool geometry and temperature field can be closely observed, thereby providing the user with control over the properties of the melt pool and the deposition process.

Thermal monitoring of the melt pool can be conducted by implementing infrared pyrometers. The temperature data from such monitoring systems can be used for making on-the-fly adjustments to process parameters or for quality assurance purposes.

Table 5.2 Summary of representative commercialized equipment for L-DED.

Company	Equipment	XYZ Travel (mm)	Degree of freedom	Laser power (W)
Optomec (USA)	LENS® 150	150 × 150 × 150	3 axes	400
	LENS® 600	600 × 400 × 400	5 axes	2000
	LENS® 800	800 × 600 × 600	5 axes	3000
	LENS® 1500	900 × 1500 × 900	5 axes	3000
	LENS® 500 HY OA	350 × 325 × 500 500 × 325 × 500	5 axes	2000
	LENS® 860 HY OA	598 × 600 × 610 860 × 600 × 610	5 axes	3000
BeAM (France)	Modulo 250	400 × 250 × 300	5 axes	500
	Modulo 400	600 × 400 × 400	5 axes	2000
	Magic 800	1200 × 800 × 800	5 axes	2000
Trumpf (Germany)	TruLaser Cell 3000	800 × 600 × 400	5 axes	8000
	TruLaser Cell 7040	4000 × 1500/ 2000 × 750/1000	5 axes	6000
FormAlloy (USA)	X & L-Series	200 × 200 × 200; 500 × 500 × 500; 1000 × 1000 × 1000	5 axes	8000
InssTek (South Korea)	MX-Lab	150 × 150 × 150	3 axes	300
	MX-600	450 × 600 × 380	5 axes	1000
	MX-1000	800 × 1000 × 650	5 axes	2000
	MX-Grande	4000 × 1000 × 1000	5 axes	3000
	MPC	300 × 300 × 200	6 axes	500
DMG Mori (Germany)	LASERTEC 65 3D	735 × 650 × 560	5 axes	2500/3000
	LASERTEC 65 3D hybrid	735 × 650 × 560	5 axes	2500/3000
	LASERTEC 125 3D hybrid	1335 × 1250 × 900	5 axes	2500/3000
	LASERTEC 4300 3D hybrid	660 × 400 × 1500	5 axes	2500/3000

Representative commercial L-DED equipment produced by industrial manufacturers, such as Optomec (USA), BeAM (France), Trumpf (Germany), DMG Mori (Germany), FormAlloy (USA), and InssTek (South Korea), and their available powders are summarized in Tables 5.2 and 5.3, respectively.

The Optomec Company provides industry-leading solutions for metal-based AM. For example, Optomec developed LENS® systems to print common engineering materials (stainless steels, tool steels, titanium alloys, cobalt alloys, etc.) and other rarer materials (zirconium, tantalum, tungsten, aluminum, bronze, refractory metals, certain ceramics, etc.). These systems correspond to a layer thickness of

Table 5.3 Summary of available powders for commercialized L-DED equipment.

Company	Available powders
Optomec (USA)	• LENS® 150, LENS® 600, LENS® 800: (Open atmosphere) stainless steel 13-8, 17-4, 304, 316, 410, 420, 15-5PH, AM355, 309, 416, IN625, IN718, IN690, pure copper, bronze, Cu-Ni, GRCOP-84, tool steel H13, S7, A-2, Stellite 6, Stellite 21, Ni-WC, Co-WC (Controlled atmosphere) CP Ti, Ti-6Al-4V, Ti6242, Ti6246, Ti4822, Ti-22Al-23Nb, Alumina, Al 4047, Waspalloy, Hastelloy X, MarM247, Rene 41, Rene 142, pure tungsten, pure molybdenum, pure niobium, TiC, CrC • LENS® 1500: Inconel alloys, stainless steels, titanium alloys • LENS® 500 HY OA: Tool steels, stainless steels, Inconels, Hastelloy, Stellite, tungsten carbide • LENS® 860 HY OA: Inconel alloys, stainless steels, cobalt, tungsten
BeAM (France)	Ti-6Al-4V, 316, Inconel 625, Inconel 718
Trumpf (Germany)	316L, CoCr, bronze, Inconel 625, Inconel 718
FormAlloy (USA)	Inconel 625, Inconel 718, Hastelloy X, Haynes 282, 316L, 15-5 PH, 17-4 PH, maraging steel, H13, Invar 36, Ti-6Al-4V, Co-Cr-Mo, pure copper, C18000, C18150, GRCop-42, GRCop-84
InssTek (South Korea)	• MX-Lab, MX-600, MX-1000, MX-Grande: CP Ti, Ti-6Al-4V, P20 steel, P21 steel, H13, 304, 316, 420, Ni600, Ni625, Ni690, Ni713, Ni718, Hastelloy 22, Hastelloy 276, Cu-Sn, bronze, CoCr, Stellite 21, Stellite 25 • MPC: Ti
DMG Mori (Germany)	• LASERTEC 65 3D, LASERTEC 65 3D hybrid, LASERTEC 125 3D hybrid: 316L, CoCr, Cu-Al, Inconel 625, PH15-5 • LASERTEC 4300 3D hybrid: Ti-6Al-4V

250–750 μm , a minimum wall thickness of 300 μm , a deposition rate of 0.5 kg/hr based on a laser power of 2 kW, and a side surface roughness of 12–25 μm . A hermetically sealed chamber is included, which can be purged with argon to maintain oxygen and moisture levels below 10 ppm. Metal powder feedstock is delivered to the deposition area through Optomec's proprietary powder feed system, which can precisely regulate the mass flow.

The LENS® systems produce near-fully dense materials with mechanical properties comparable to or superior to those of cast materials and, in some cases, forged materials. To overcome the issues of low printing resolution and poor surface

quality, L-DED and subtractive manufacturing capabilities are integrated into machines, such as the LENS HY OA series (Optomec) and LASERTEC 3D hybrid series (DMG Mori).

5.7 Microstructure and Mechanical Properties

The microstructural characteristics (e.g. grain morphology and size) of L-DED parts are highly sensitive to their thermal history during the deposition process, which may involve high heating/cooling rates, significant temperature gradients, and complex thermal cycles. Therefore, predicting the microstructures of L-DED parts and their degree of dependence on the process parameters is highly challenging, and overcoming such a challenge is vital for establishing effective microstructural control of L-DED parts with superior mechanical properties.

The solidification mechanisms involved in LPBF are also applicable in L-DED. The temperature gradient G and growth rate R affect the solidification process. They contribute to three major kinds of microstructural morphology within L-DED parts: columnar, columnar + equiaxed, and equiaxed grain morphology. A high temperature gradient promotes the transition of equiaxed grains to columnar grains, and increasing the cooling rate, given by $G \times R$, results in a finer microstructure. For thin-walled parts fabricated via L-DED, the ranges of G and $G \times R$ are approximately 100–200 K/mm and 200–6000 K/s, respectively (Hofmeister et al. 1999). Optimal G and R values depend on the material properties, process parameters, part geometry, printing strategies, environmental/machine conditions, etc. The tensile properties of various metal powder materials printed through L-DED are summarized in Table 5.4.

5.7.1 Titanium and Its Alloys

The microstructural evolution of Ti-6Al-4V parts printed by L-DED strongly depends on the process parameters (e.g. laser power and laser scanning speed), printing strategy, part geometry, and intrinsic properties of the materials involved (e.g. thermal conductivity of the printed material and substrate). The microstructure of such Ti-6Al-4V parts commonly consists of α/α' phases present in a β matrix, namely, primary α , secondary α , plate-like α , colony α , acicular martensite α' , and Widmanstätten and basket-weave structures.

In a study, the crystallographic microstructure within a β matrix comprises the acicular martensitic α' phase, a large number of Widmanstätten α -laths structures, and a few β phases between the α -laths (Li et al. 2015). Figure 5.6a,b show needle-like martensitic α' clusters and Widmanstätten α -laths. Within the β grains, the Widmanstätten α -laths structures display basket-weave morphology. Both the needle-like martensitic α' -phase clusters and Widmanstätten α -laths exhibit thin and needle-shaped microstructures, which correspond to high strength levels.

Table 5.4 Summary of the tensile properties of various metal materials printed by L-DED.

Material	Yield strength (MPa)	Ultimate tensile strength (MPa)	Elongation (%)
304L ^{a)}	337	609	48.2
316 ^{b)}	558	639	21
316L ^{c)}	576	776	33
316L ^{d)}	405–415	620–660	32–40
17-4 PH ^{e)}	758	1129	14.1
Fe19Ni5Ti ^{f)}	—	>1300	>10
AISI 4340 steel ^{g)}	—	1398.65	1.665
1Cr12Ni2WMoVNB ^{h)}	—	1227	7.7
Inconel 718 ⁱ⁾	750	958	17
Inconel 718 ^{j)}	1024	1334	34.1
Inconel 718 ^{k)}	752.17	1074.19	22.46
Inconel 738 ^{l)}	1350	1392	1.13
Inconel 625 ^{m)}	531	840	16
Haynes 282 ⁿ⁾	633	943	31.6
Ti–6Al–4V ^{o)}	961	1072	17
Ti–6Al–4V ^{p)}	945	1041	14.5
Ti–6Al–4V ^{q)}	1094	1137	4.7
Ti–6Al–2Sn–4Zr–2Mo–0.1Si ^{r)}	976	1021	8.45
Ti–4Al–1.5Mn ^{s)}	855	912	10.2
NiTi ^{t)}	400	480	1.6
TiAl ^{u)}	421	539	1.7
Al–Si10–Mg ^{v)}	—	355	8.1

a) (Wang et al. 2016);

b) (Zhang et al. 2014);

c) (Ziętala et al. 2016);

d) (Yadollahi et al. 2015);

e) (Yu et al. 2020);

f) (Kürnsteiner et al. 2020);

g) (Sun et al. 2015);

h) (Wang et al. 2010);

i) (Wang and Shi 2020);

j) (Zhang et al. 2020);

k) (Li et al. 2020);

l) (Ramakrishnan and Dinda 2019a);

m) (Zhang et al. 2016);

n) (Ramakrishnan and Dinda 2019b);

o) (Keist and Palmer 2016);

p) (Carroll et al. 2015);

q) (Todaro et al. 2020);

r) (Wang et al. 2020);

s) (Tian et al. 2014);

t) (Bimber et al. 2016);

u) (Thomas et al. 2017);

v) (Wang et al. 2019).

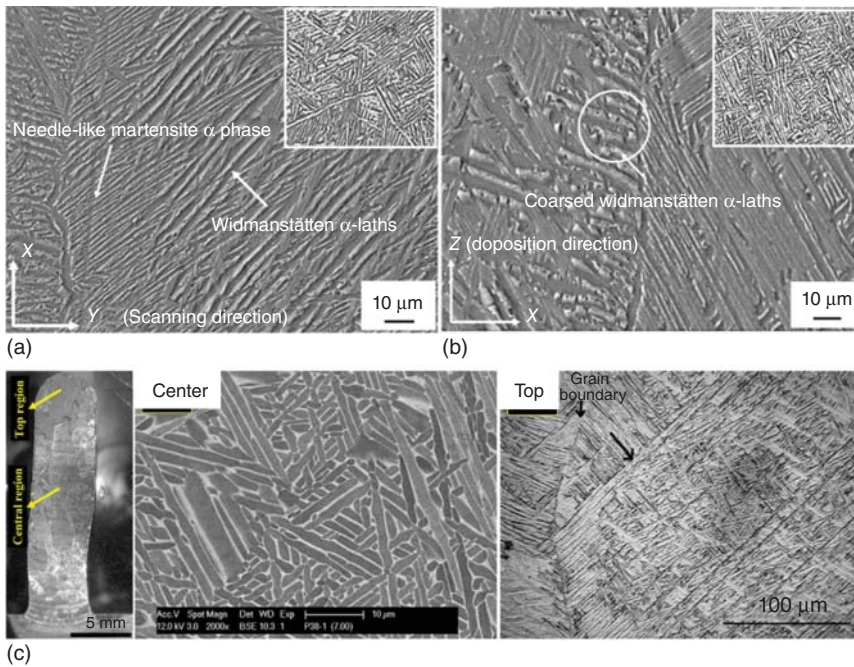


Figure 5.6 Microstructure of Ti-6Al-4V parts fabricated by L-DED. (a) In the x - y plane and (b) in the x - z plane. Source: Li et al. (2015)/reproduced with permission from Elsevier. (c) Different regions along the build direction. Source: Baufeld et al. (2011)/reproduced with permission from Elsevier.

Coarse Widmanstätten α -laths can also be observed along the β grain boundaries. The coarse α -laths reduce the strength of the material by weakening the inhibition effect of gliding dislocations. When a high density of α -lamellae precipitates exists along the β grain boundaries, the dislocations glide smoothly, and the yield strength of the material decreases consequently.

The grid structures shown in Figure 5.6c was considered as a martensitic phase (Baufeld et al. 2011). In general, slow cooling leads to the formation of colony structures, while rapid cooling results in the formation of basket-weave structures and induces martensitic transformation. The diversity of microstructures suggests that the microstructural evolution during the L-DED process is controlled by the rate of the final cooling from the β -transus temperature to the ambient temperature. Notably, thermal cycles below the β -transus temperature may have little to no impact on the microstructure. The martensitic α' structure can subsequently transform into a fine lamellar $\alpha + \beta$ microstructure through the annealing treatment at a temperature of 700–850 °C.

Post-AM stress-relief treatment is generally recommended for aerospace components printed via L-DED. Such treatment of Ti-6Al-4V parts is typically performed at temperatures below 995 °C in the $\alpha + \beta$ regions, which does not significantly impact prior β grains but alters the distribution, size, and morphology of the α -phase (Åkerfeldt et al. 2016). Heat treatment at temperatures higher than 995 °C leads to

complete dissolution of the α phase and transformation of the morphology of prior β grains from columnar to globular.

A comparative study was conducted to investigate pure titanium parts manufactured by L-DED, LPBF, and casting processes. An analysis of the processing parameters indicated that significantly higher laser power is required in L-DED than in LPBF to obtain a near-full density of the printed parts. The pure titanium parts underwent an allotropic phase transformation at a temperature of approximately 865 °C, at which the $\alpha \rightarrow \beta \rightarrow \alpha$ transformation occurs during the heating and cooling processes (Gey and Humbert 2002). Figure 5.7 displays the microstructures of the pure titanium samples fabricated by L-DED, LPBF, and casting processes (Attar et al. 2017).

The as-cast titanium sample possessed a microstructure containing a mixture of serrated α and fine acicular α phases (Figure 5.7a). In contrast, the LPBF sample exhibited a dominant martensitic α' phase with lath-type morphology and fine acicular α' phase in certain regions (Figure 5.7b). In addition, an α matrix embedded with plate-like α phases and Widmanstätten structures was observed in the L-DED samples (Figure 5.7c,d). The melt pool tracks were not visible in the microstructure of pure titanium parts printed by L-DED and LPBF since using pure titanium eliminated compositional segregation or phase variations across the individual tracks. The unique morphology can be attributed to the different cooling

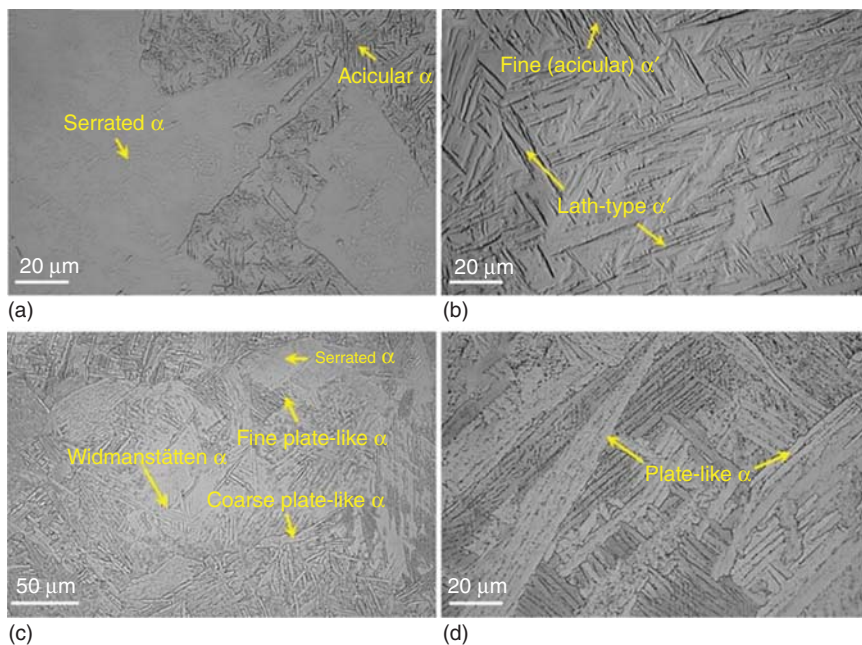


Figure 5.7 Optical images showing microstructures of commercially pure Ti processed by (a) casting, (b) LPBF, and (c, d) L-DED. Source: Attar et al. (2017)/reproduced with permission from Elsevier.

rates required for its formation, i.e. 10^3 K/s for the lath type (Oh et al. 2004) and 10^5 – 10^6 K/s for the fine acicular type (Yang et al. 2016).

Regarding tensile properties, the Ti–6Al–4V alloy printed by L-DED could achieve a high ultimate tensile strength of 900–1200 MPa. The values of elongation at failure for printed Ti–6Al–4V parts along the transversal direction (x – y plane) may be 25–33% higher than those along the longitudinal direction (z direction) (Keist and Palmer 2016). The lower ductility of the parts along the longitudinal direction was attributed to the β grain boundaries typically aligning perpendicular to the transverse direction, which allows easier crack propagation.

The mechanical properties of a Ti–6Al–4V part printed by L-DED also vary locally along the distance from the substrate. For example, the region close to the top surface of the part can efficiently transfer heat to its ambient environment and undergo fewer thermal shocks from the deposition of subsequent layers. In contrast, the region near the substrate is subjected to more remelting and thermal cycles, and it has a greater heat flux due to conduction from the top layer to the substrate during the printing process.

Figure 5.8 presents the mechanical properties of the specimens tested along the (010), (100), and (001) orientations (Wolff et al. 2016). For both specimens corresponding to the (001) and (010) directions, a clear trend of tensile strength increasing with the distance from the cubic surface can be observed. Meanwhile, the elongation to failure decreases significantly. The specimens tested along the (100) direction exhibited greater strength and elongation.

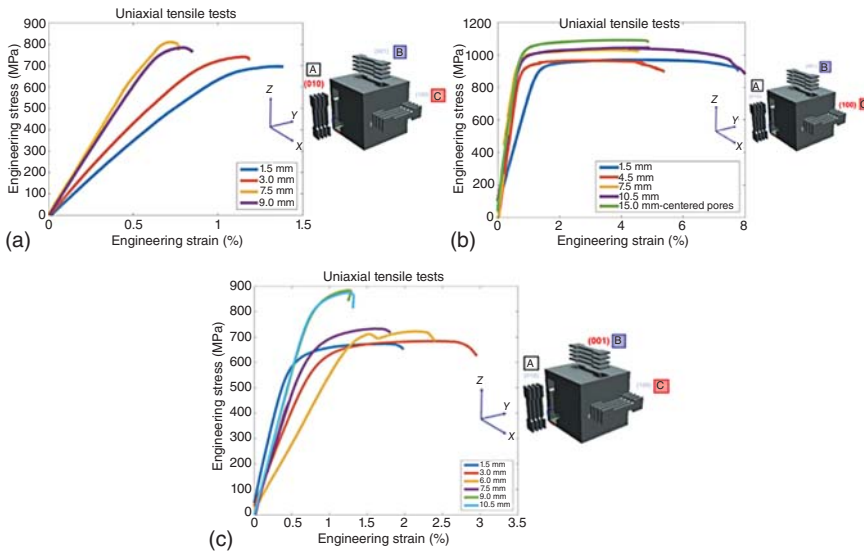


Figure 5.8 Stress–strain curves of a Ti–6Al–4V alloy printed by L-DED for different specimen orientations and different distances from the surface of a cubic part. (a) (010), (b) (100), and (c) (001). Source: Wolff et al. (2016)/reproduced with permission from Elsevier.

The hardness of a Ti-6Al-4V alloy printed by L-DED strongly depends on its thermal history (i.e. temperature, cooling rate, and heat accumulation), which can be manipulated by varying process parameters. The relationship between the microstructure and hardness of an L-DED-printed Ti-6Al-4V part has been investigated (Paydas et al. 2015). Regions with high hardness values of around 350–370 HV were attributed to the martensitic phases formed after rapid cooling, and regions with lower hardness values of 315–350 HV corresponded to the Widmanstätten structure formed at lower cooling rates.

The hardness and microstructure of a prior β grain are functions of the cooling rate of the material below its β -transus temperature instead of the heating duration at temperatures above it (Brandl and Greitemeier 2012). A solution heat treatment at 1200 °C with different heating durations, followed by water quenching from above the β -transus temperature, all resulted in a similar microstructure of basket-weave α and/or martensitic α' , with a microhardness of 333–346 HV. Conversely, a solution heat treatment at 1200 °C for two hours followed by furnace cooling has been determined to substantially decrease the hardness values by introducing the coarsened prior β grains and α -lamellae. On the other hand, heating at 600 °C for four hours followed by furnace cooling was found to increase the average hardness of the printed part due to the precipitation of the Ti_3Al phase (Baufeld et al. 2011).

The melting, solidification, and local thermal history of L-DED parts strongly depend on the laser power and scanning speed. A high laser power usually corresponds to high energy input and low cooling rate, giving rise to the formation of large grain sizes and coarse columnar or lamellar grains. Such large grains decrease the strength and hardness of the printed part. Moreover, high laser power reduces the volume fraction of the martensitic phase as a result of lower cooling rates, thereby improving the ductility and fatigue behavior of the printed part (Zhai et al. 2016).

The powder flow rate directly determines the amount of powder deposited per unit time, which influences the layer thickness and the resultant microstructure of the printed part. A combination of high laser power and low feed rate can effectively suppress the generation of lack-of-fusion pores by ensuring complete melting of the powder.

An increase in the scanning speed or a decrease in the incident energy increases the thermal gradient and cooling rate. Such changes may lead to refinement of the lamellar structures and facilitate the evolution of a finer microstructure with a higher volume fraction of the martensitic phase, dislocations, and grain boundaries, thereby hardening the material (Mok et al. 2008). However, a high scanning speed may weaken the bonds between the deposited layers and consequently degrade the mechanical properties of the printed part. In contrast, a low scanning speed prolongs the interaction between the melt pool and the laser, resulting in a large melt pool that can effectively fuse the deposited layers upon solidification.

5.7.2 Nickel Alloys

The microstructures of Inconel 718 parts printed by L-DED with different laser power values are compared in Figure 5.9a,b. Fine equiaxed grains were observed

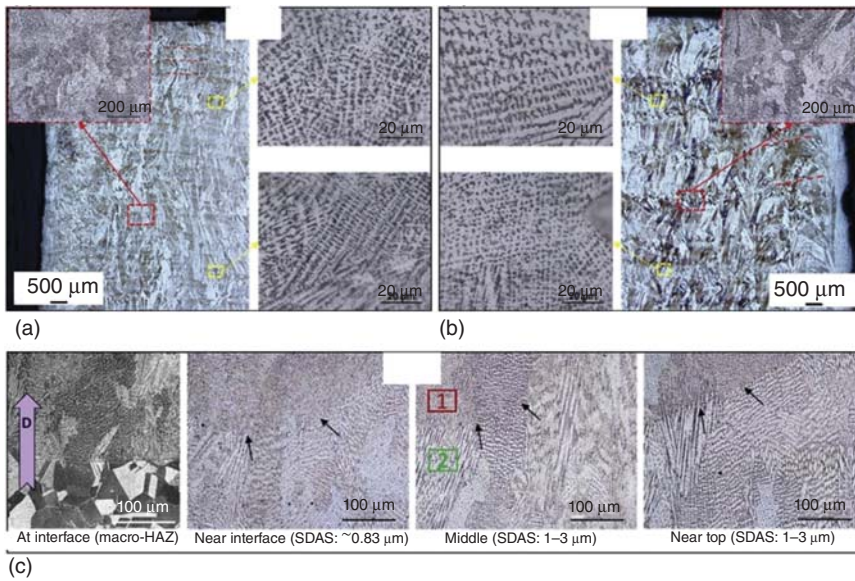


Figure 5.9 Microstructures of Inconel 718 parts fabricated by L-DED under (a) low and (b) high laser power and (c) variation in the microstructure from the bottom to the top of a low-power build. Source: Zhai et al. (2019)/reproduced with permission from Elsevier.

in their layer boundaries/heat-affected zones (HAZs), and columnar grains were distributed within the layers of Inconel 718 samples prepared at both low and high laser power values. In both cases, the columnar grains within the layers were of similar sizes, and a similar dendritic microstructure was observed at higher magnification values. No distinguishable HAZs were found in the top region of the samples fabricated at low laser power, as shown in Figure 5.9c. Meanwhile, finer dendrites were observed in the region close to the substrate with a secondary dendrite arm spacing (SDAS) of $\sim 0.83 \mu\text{m}$. Coarser dendrites toward the top of the sample had an SDAS of $\sim 3 \mu\text{m}$.

Inconel 718 parts fabricated by L-DED exhibited a banded grain structure, with fine grain zones at the interfaces between their layers containing inclined columnar grains (Figure 5.10a). The fine grain band size of the parts was $150\text{--}200 \mu\text{m}$ at their base, and it decreased to $20 \mu\text{m}$ at their top. Such a decrease is attributed to the increase in heat accumulation along the build height, which reduces the cooling rate of newly deposited layers and suppresses the formation of fine grains along the build direction.

The fine grain region possessed a more randomized texture than the columnar grains (mainly $\langle 001 \rangle$ oriented grains and few frequently $\langle 101 \rangle$ oriented grains along the y direction). However, the samples exhibited an overall complex randomized texture. Their inverse pole figure (IPF) maps also indicated a banded structure with randomly oriented grains (Figure 5.10b). Such a banded structure was attributed to the layer-wise deposition process, in which remelted regions experienced rapid cooling under a high temperature gradient. Consequently, fine equiaxial

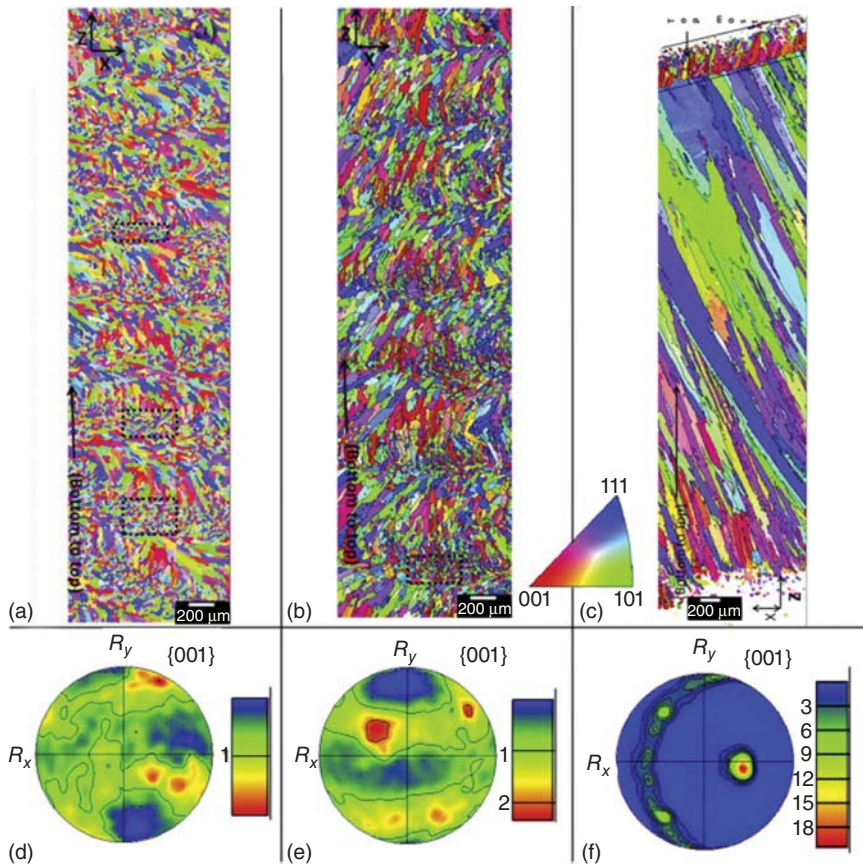


Figure 5.10 Electron backscatter diffraction (EBSD) results displaying the texture of Inconel 718 parts printed by L-DED using different scanning strategies. (a) Unidirectional deposition, (b) bidirectional deposition, (c) bidirectional high-power deposition, and (d–f) their respective pole figures. Source: Parimi et al. (2014)/reproduced with permission from Elsevier.

grains were formed in such regions, while the deposited layers were subjected to relatively slow cooling and formed columnar grains.

Figure 5.10c shows that the build initially began with small columnar grains, which progressively grew larger along the build direction. The appearance of small columnar grains was prominent in the final layers and can be ascribed to the rapid heat transfer between the final layers and the ambient atmosphere. The $\{001\}$ pole figures of samples indicate a generally weak texture in Figure 5.10d,e. Figure 5.10f indicates that the grains were characteristic of a directionally solidified structure with a preferred orientation. These grains grew epitaxially parallel to the $\{001\}$ planes, along the direction of the maximum thermal gradient and the favored crystallographic orientation of a face-centered cubic (FCC) structure. The grains tilted toward the resultant heat flux direction (from the sides of the part to its center)

as the sides exhibited a higher cooling rate than the center due to heat transfer to the ambient environment via conduction and convection.

The as-deposited Inconel 718 alloy displayed a yield strength of 752 MPa, an ultimate tensile strength of 1047 MPa, and an elongation of 22.46% (Li et al. 2020). The L-DED process induced the precipitation of the γ'' and γ' strengthening phases. The precipitation strengthening and interactions between the precipitates and the dislocations improved the yield strength of the as-deposited L-DED samples. As a result, the yield strength and elongation of the samples were comparable to those of parts fabricated by LPBF.

Inconel 625 parts fabricated by L-DED possessed a unique microstructure in which only columnar grains and primary dendrites were observed at the bottom of each layer (Dinda et al. 2009). The top of the layers displayed a fine dendritic microstructure with secondary arms, as shown in Figure 5.11. It exhibited a slower cooling rate than the bottom of the layers, which allowed for the growth of secondary dendrites. Therefore, a gradual columnar–dendritic microstructural change was observed from the bottom to the top of each layer. The average primary dendrite spacing at the bottom of each layer was approximately 5 μm , and the secondary arm spacing at the top varied between 1.5 and 2.5 μm .

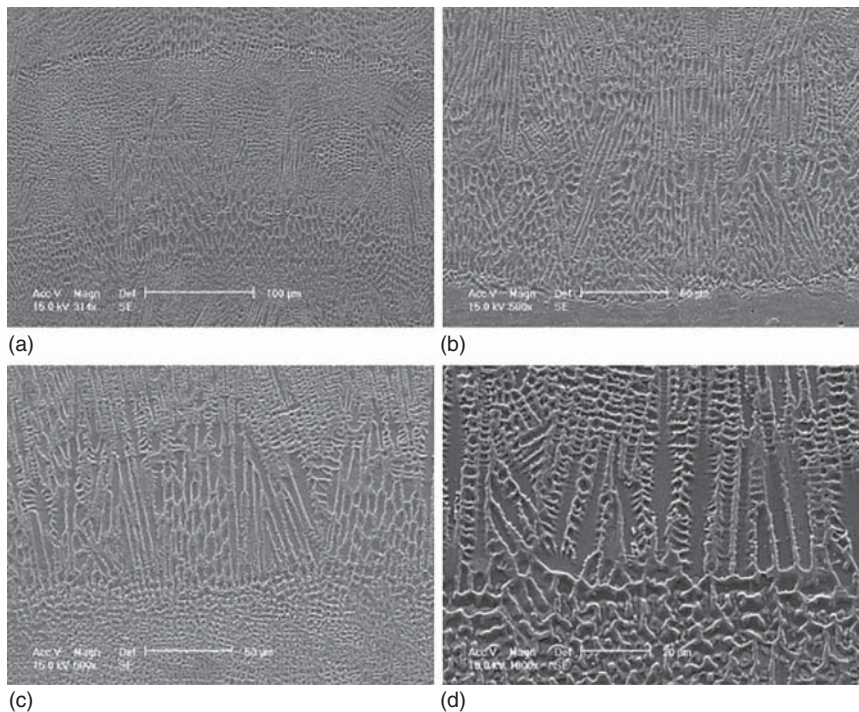


Figure 5.11 Different locations of the microstructure of a single-layer Inconel-625 sample. (a) First layer, (b) second layer, (c) third layer, and (4) fourth layer. Source: Dinda et al. (2009)/reproduced with permission from Elsevier.

The overall microstructure of the as-printed sample was composed of a nickel-based δ phase along with MC, M_6C , and $M_{23}C_6$ carbides (M represents metal elements). The formation of the Nb-rich MC phase was attributed to the rapid solidification process in L-DED, and these phases were mainly present in the interdendritic regions. While the formation of M_6C and $M_{23}C_6$ was attributed to the exposure of solidified materials at elevated temperatures, the formation of MC phases depended on the formation of carbides during solidification, growth of primary carbides, and high-temperature exposure of previously solidified materials.

Inconel 625 alloys fabricated by L-DED can achieve an ultimate tensile strength of ~ 920 MPa, a yield strength of ~ 570 MPa, an elongation of 48%, and a Charpy impact resistance of 104 J (Paul et al. 2007). It was established that the laser scanning pattern does not significantly affect the mechanical properties of Inconel 625 parts. Fracture toughness values ranging from 200 to 255 kJ/m² were obtained, and the printed samples could display stable crack growth (Ganesh et al. 2010). In another study, the impact energy of Inconel 625 specimens showed a slight increase after solution treatment (Puppala et al. 2014). The average microhardness of IN625 was measured to be 275 HV at room temperature and 235.7, 214.7, and 202.8 HV at elevated temperatures of 550, 600, and 650 °C, respectively.

5.7.3 Iron Alloys

Austenitic stainless steels, such as 304L and 316L, have been extensively fabricated by L-DED for their excellent combination of strength, ductility, and high corrosion resistance. However, such materials can potentially undergo a deformation-induced phase transformation from an FCC austenitic phase to a body-centered cubic (BCC) martensitic phase under loading. This microstructural transformation results in a material displaying a high strain hardening rate on the macroscale, which endows it with a good synergy of strength and ductility.

In a study by Weng et al., the microstructure of 316L printed by L-DED was determined to be composed of dominant austenite and intergranular skeletal ferrite (Weng et al. 2019). The microstructure of the outer layer of the deposited sample differed from that of its inner region with a transition zone between them, as annotated in Figure 5.12a,b,e,f. The inner region exhibited a dual-phase microstructure comprising dominant austenite γ and inter ferrite δ phases (Figure 5.12c,d,g), while the outer layer contained regular austenite grains (Figure 5.12h). The inhomogeneity in the microstructure is attributed to the Gaussian energy distribution of the laser beam and different cooling conditions in different regions of the sample. It is reasonable to assume that the outer layer was subjected to a lower peak temperature and faster cooling than the inner region when exposed to the laser beam.

The effects of processing parameters on the mechanical properties of 304L stainless steel walls fabricated using L-DED have also been investigated (Wang et al. 2016). Columnar δ -ferrite dendrites were observed to be distributed within the austenite matrix. During the rapid solidification of the austenitic stainless steel, the transformation of δ -ferrite to austenite was seldom fully complete, resulting in

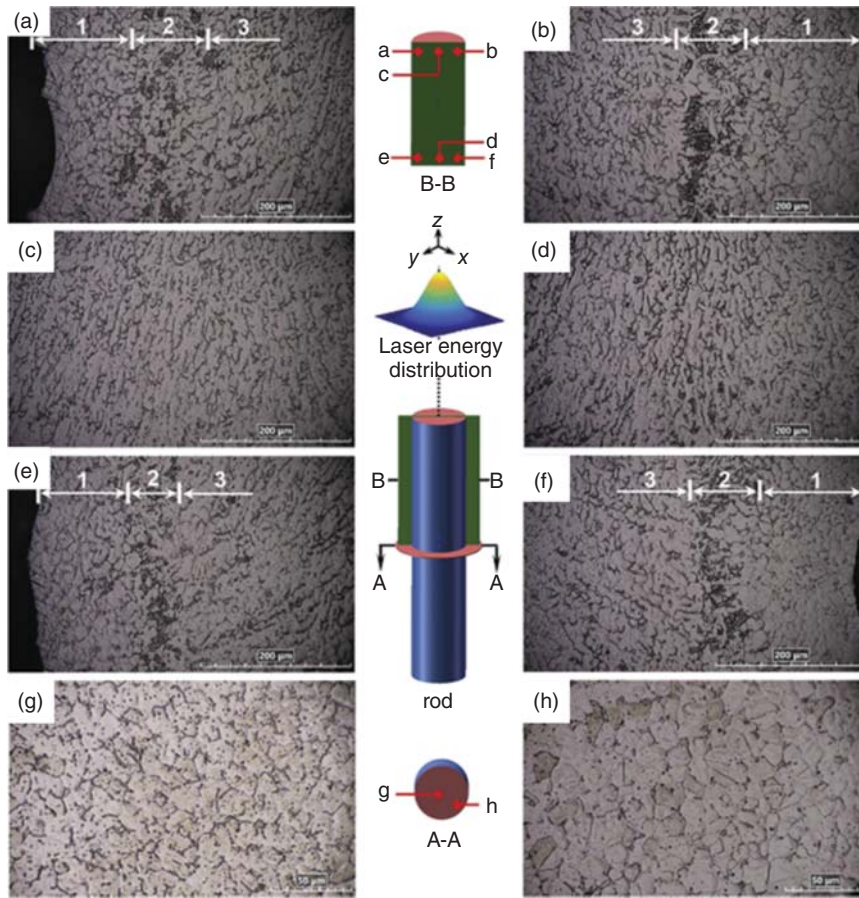


Figure 5.12 Different positions of the microstructure of a 316L part printed by L-DED. (a) Position a, (b) position b, (c) position c, (d) position d, (e) position e, (f) position f, (g) position g, and (h) position h. 1, 2, and 3 indicate the outer layer, transition zone, and internal positions, respectively. The deposited rods were cut into two equal parts, and the upper part was cut longitudinally. Source: Weng et al. (2019)/reproduced with permission from Elsevier.

the formation of residual ferrite dendrites in the austenite matrix upon solidification. At the bottom of the walls, columnar grains that grew along the direction of the predominant heat flow path were formed, which was attributed to the deposition of subsequent printing layers. The grains were more randomly oriented at the top of the walls, resembling an equiaxed texture.

316, 316L, and 304L stainless steel parts produced by L-DED were found to exhibit lower tensile strength when the applied tensile loading direction is parallel to the build direction than when it is normal to the build direction. This physical property was attributed to the different types of microstructures formed.

In one of the studies, a 304L alloy printed by L-DED exhibited an ultimate tensile strength of 734 MPa, a yield strength of 553 MPa, and an elongation of 50%

(Smith et al. 2019). The strength of the printed 304L part was similar to that of its strain-hardened forged counterpart and exceeded the minimum value of a standard annealed wrought 304L part. The high density of dislocations in the printed 304L part led to a yield strength increase of 166–191 MPa, while compositional micro-segregation was predicted to contribute an additional yield strength of 123–135 MPa. A combination of high strength and elongation can be obtained with a careful selection of process parameters to eliminate defects.

L-DED has also been utilized to develop precipitation-hardened maraging steel alloys because of its intrinsic capacity for multi-material printing (Kürnsteiner et al. 2017). Fe–19Ni– x Al graded samples were produced with x ranging from 0 to 25 at%, as shown in Figure 5.13a. Their compositionally graded structure revealed the effect of aluminum addition on their microstructure. Notably, a coarse-grained ferritic microstructure was formed when the aluminum concentration was above

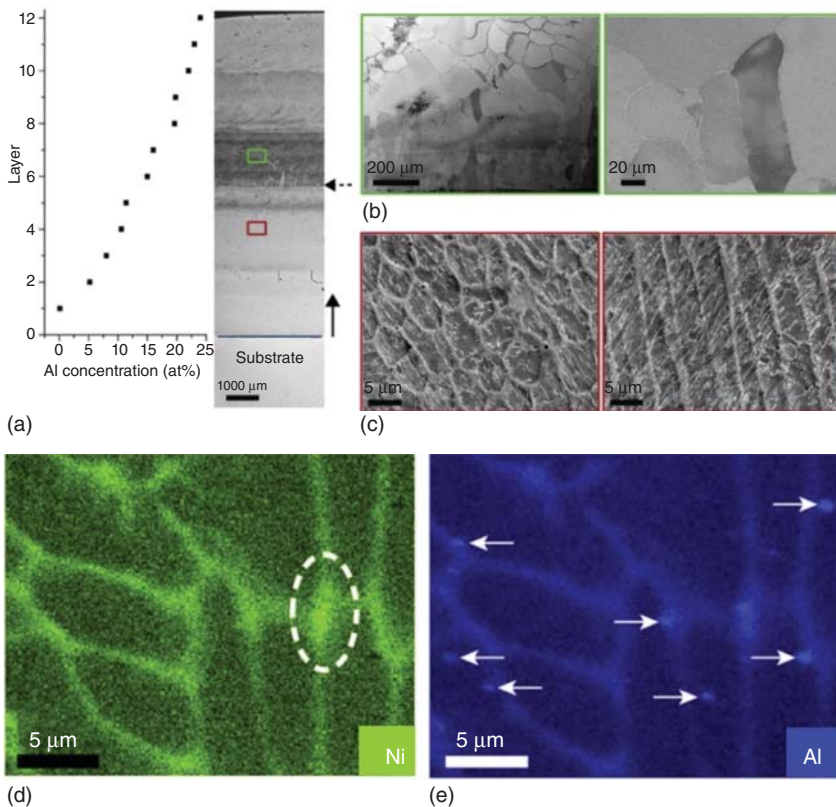


Figure 5.13 (a) Overview of a compositionally graded Fe–19Ni– x Al structure, illustrated by Al concentration plotted against the layer number and the corresponding optical microscope (OM) image, (b) SEM images of coarse-grained ferritic regions with 15 at% Al, and (c) SEM images of fine-grained martensitic regions with 10 at% Al. Energy dispersive spectroscopy (EDS) mappings of the regions with 10 at% Al showing the enrichment of (d) Ni and (e) Al at dendrite boundaries. Source: Kürnsteiner et al. (2017)/reproduced with permission from Elsevier.

15 at% (Figure 5.13b). Meanwhile, a fine-grained martensitic microstructure with fine cellular dendrites was obtained for aluminum concentration below 15 at% (Figure 5.13c).

In the Fe–19Ni– x Al graded samples, nickel and aluminum atoms were segregated at the dendrite boundaries during solidification, as shown in Figure 5.13d,e. Additionally, nano-scaled aluminum oxide particles were induced in the martensitic microstructure. Al-rich precipitates began to form once the aluminum content exceeded 5 at%, and the density of precipitation increased with the aluminum concentration. In the compositionally graded samples with an aluminum content ranging from 0 to 25 at%, a martensitic structure was observed up to 15 at% aluminum. A minimum of 5 at% aluminum was required to induce precipitation strengthening.

The layer-wise manufacturing process of L-DED enables the tailoring of the microstructures of the printed samples. A Fe19Ni5Ti bulk sample with hard (dark areas) and soft zones (bright areas) was produced (Figure 5.14a) through idle cooling and cyclic heating (Kürsteiner et al. 2020), as shown in Figure 5.14b. This compound sample with hard and soft layers (akin to Damascus steel) exhibited enhanced ultimate strength and elongation compared to samples fabricated without interval cooling (Figure 5.14c). The high cooling rate of L-DED allows maraging steels to accommodate a soft martensitic matrix with retained austenite.

The fractions of martensite and austenite in both the hard and soft regions were found to be similar (Figure 5.14d). Note that the martensitic matrix was formed during the internal cooling stage. Subsequent deposition of layers triggered precipitation within the martensite (Figure 5.14e), inducing a high density of precipitates within the martensitic matrix (Figure 5.14g). Meanwhile, titanium atoms were embedded in the austenite and served as a stabilizer (Figure 5.14f). The thermal history of the sample was adjusted through proper pauses at certain deposited layers to control the martensite transformation and achieve *in situ* precipitation strengthening. Such an approach can be extended to fabricating other precipitation-hardened alloys through metal powder-based AM methods.

5.7.4 Others

5.7.4.1 Aluminum Alloys

Research on aluminum alloys printed by L-DED is limited and encounters more challenges than studies based on LPBF. First, aluminum is characterized by a high surface reflectivity and high thermal conductivity, which are unfavorable for material deposition and melt pool formation. Thus, a high laser energy density is required to create and stabilize the melt pool. Second, an excessively high energy density may promote the evaporation of alloy elements with low boiling points, such as zinc and magnesium, which are commonly present in aluminum alloys. The evaporation of such elements can result in material loss, formation of gas pores, and degradation of the mechanical properties of the deposited aluminum alloy. As a result, fluctuations in the alloy composition and hot cracking may occur easily. Third, due to the wide range of solidification temperatures and high thermal expansion coefficients of

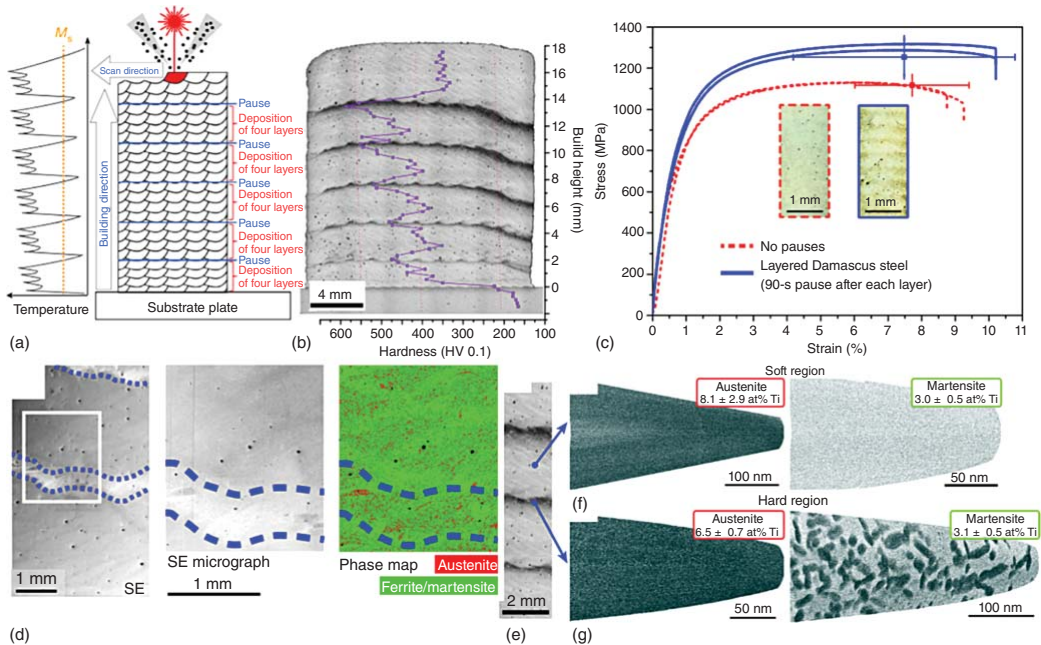


Figure 5.14 (a) Schematic of an L-DED process, including a simple sketch of the temperature profile. The process was paused for the sample to cool after four layers were built. (b) OM image showing the dark zones at the pause positions and their corresponding hardness profiles. (c) Tensile stress-strain responses. (d) SEM image featuring the hard and soft regions and their corresponding phase maps. Atom probe tomography results: (e) OM image indicating the detected positions and Ti atom maps for austenite and martensite in the (f) soft and (g) hard regions. Source: Kürnsteiner et al. (2020)/reproduced with permission from Springer Nature.

aluminum alloys, rapid solidification may be associated with high levels of residual stresses, culminating in cracking and deformation of the as-printed parts. Finally, the low density of aluminum alloys easily makes the powder fly before melting.

A thin-wall Al–Si10–Mg alloy fabricated by L-DED achieved a tensile strength of 360 MPa, an elongation of 12.7%, and it possessed a microstructure consisting of α -aluminum dendrites and eutectic silicon (Wang et al. 2019). In each layer of the Al–Si10–Mg alloy, three representative zones were observed (Figure 5.15a). A fine columnar dendrite zone was created in the upper region of the melt pool due to sufficient heat being dissipated to the atmosphere and previously deposited layers (Figure 5.15b). Meanwhile, a coarse columnar dendrite zone was formed at the bottom of the melt pool due to a low cooling rate, which was attributed to heat supplied by the upper part of the melt pool and heat accumulation in the preceding layers (Figure 5.15c).

The HAZ was induced by the thermal attack from newly deposited layers to previously deposited layers, which acted as an intrinsic heat treatment leading to the precipitation of silicon particles along the aluminum–silicon boundary and their subsequent spheroidization (Figure 5.15d). As a result, a rod-like phase was formed under a high energy input (Figure 5.15e). It comprised a series of small columnar dendrites surrounded by severely altered cellular dendrites (Figure 5.15f).

The densification of an Al–Si10–Mg part fabricated by L-DED is significantly affected by the oxygen concentration of the atmosphere, which is a more prominent factor in L-DED than in LPBF. Its porosity increased to 1.89% under an oxygen level of 900 ppm (Figure 5.15g), and its mechanical properties were modified by changing the SDAS under different heat input values. As the laser power increased from 480 to 910 W, a smaller SDAS was induced under the increased cooling rate, resulting in enhanced strength and elongation of the printed part (Figure 5.15h).

Preheating treatment was applied to the sample printed with a laser power of 1200 W. The cooling rate was reduced due to the suppressed temperature gradient, leading to reduced residual stress and mechanical strength. The microstructure of Al 5083 fabricated by L-DED consisted of both equiaxed and columnar grains, which comprised a small amount of pure hexagonal close packed (HCP)-magnesium phase surrounded by a matrix composed of the FCC-aluminum phase (Svetlizky et al. 2020). The deposited alloy exhibited an ultimate tensile strength of 244 MPa, a yield strength of 117 MPa, and an elongation of 18.3%.

5.7.4.2 Copper and Its Alloys

L-DED has been applied to print pure copper, copper–nickel, GRCo-84, nickel–aluminum–bronze (NAB) alloys, etc. A Cu–9Al–5Fe–5Ni alloy was fabricated through L-DED, which achieved a density of over 99% and a high tensile strength of 769–949 MPa (Li et al. 2021). The microstructure of the printed alloy consisted of a metastable martensite β^* phase, a Widmanstätten α phase, and Fe_3Al and NiAl nanoprecipitates (Figure 5.16). In addition, the samples possessed a hierarchical microstructure comprising microscale cellular structures, sub-microscale grains, and nanoscale precipitates and twins.

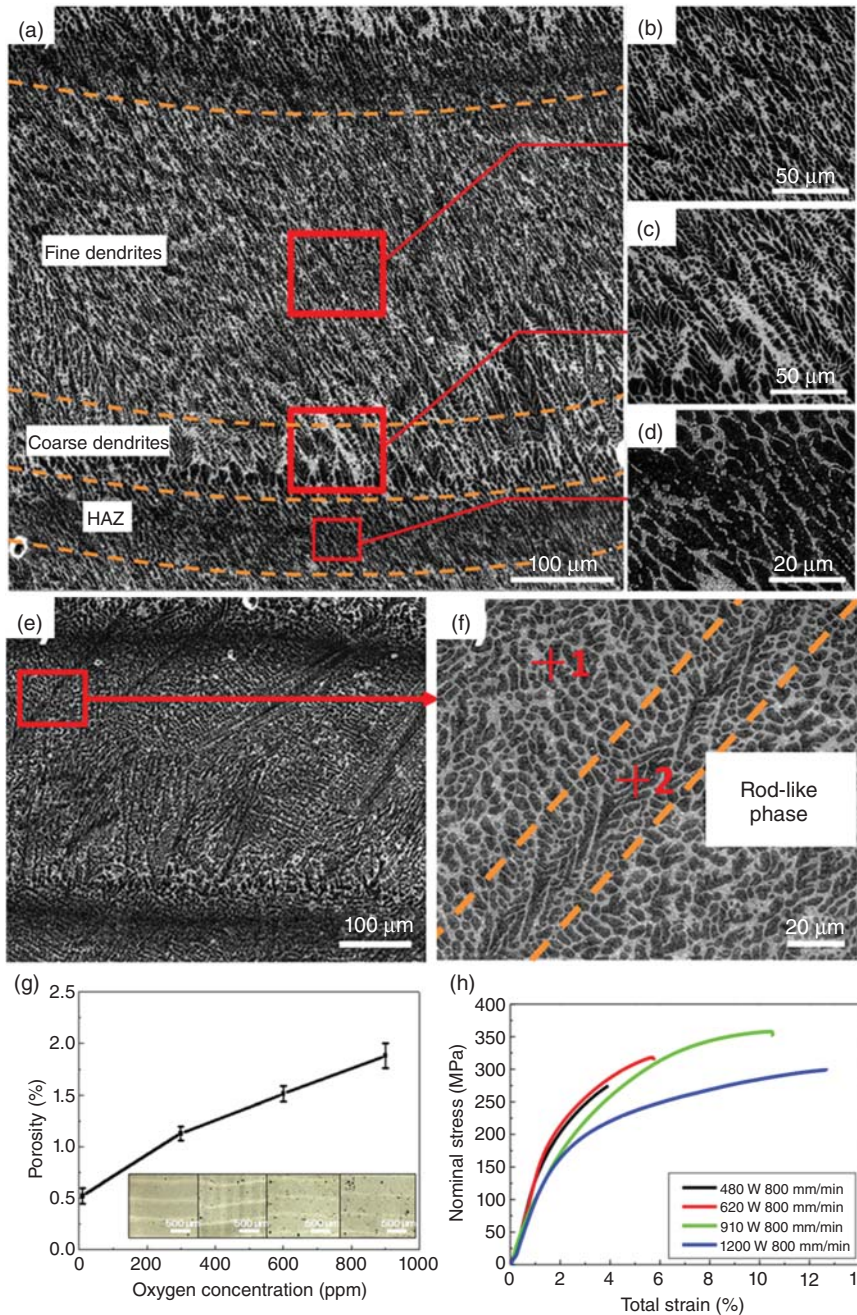


Figure 5.15 (a) SEM image of deposited Al-Si10-Mg with a heat input of 480 W and an enlarged view of its (b) fine columnar dendrite zone, (c) coarse dendrite zone, and (d) HAZ. (e) SEM image of the sample with a heat input of 1200 W and (f) an enlarged view of its rod-like phase. (g) Effect of oxygen concentration on porosity and the corresponding optical micrograph and (h) stress-strain curves with different heat input values. Source: Wang et al. (2019)/reproduced with permission from Taylor & Francis Group.

The cellular structures consisted of strong β^* phases and ductile α phases distributed at the boundaries of β^* grains (Figure 5.16a,b), which contributed to the high strength and ductility of the printed alloy. In particular, a cellular structure with dimensions of 20–40 μm facilitated Hall–Petch type strengthening through the highly dense α/β^* boundaries. The Fe_3Al and NiAl precipitates formed a core/shell structure with a radius of ~ 50 nm, which was attributed to their similar FCC crystal structures and low lattice mismatch (Figure 5.16c). The high density of hard precipitates impeded dislocation slip, which led to precipitation strengthening.

Aluminum was enriched in the boundaries of adjacent β^* plates, thereby reducing the stacking fault energy (SFE) (Figure 5.16e). As a result, nanotwins were formed at the boundaries of β^* plates (Figure 5.16d). The twin boundaries comprised partial dislocations, which facilitated dislocation strengthening, and the alloying elements (aluminum, iron, and nickel) in the copper matrix also contributed to solid solution strengthening.

Because of the synergistic effects of the Hall–Petch type strengthening, precipitation strengthening, dislocation strengthening, and solid solution strengthening, the printed alloy possessed a yield strength of 713 MPa, which was 160% higher than its cast counterparts (Figure 5.16f). It also exhibited high strength and good ductility compared to its counterparts prepared by other AM processes.

L-DED is also widely applied in the fabrication of multi-materials such as copper/steel and copper/nickel to harness the corrosion resistance and high thermal conductivity of copper. For example, a copper/steel multi-material was manufactured via L-DED using NAB and 15-5 PH powders, which incorporates the superior corrosion resistance of NAB and the outstanding mechanical performance of 15-5 PH (Figure 5.17a) (Li et al. 2022).

The NAB/15-5 PH interface, which consisted of an interlayer of Fe_xAl dendrites, contained no cracks or lack-of-fusion defects (Figure 5.17b,c). The NAB region comprised equiaxed grains with weak textures, while the 15-5 PH region exhibited columnar dendritic grains growing epitaxially along the build direction (Figure 5.17c). Compared to other copper/steel multi-materials fabricated by AM, the multi-material sample displayed a high ultimate tensile strength of 754.6 MPa in the transverse direction and 854.6 MPa in the longitudinal direction (Figure 5.17e).

In an oceanic environment, a thick passive film was formed on the NAB surface, protecting the underlying material from corrosion. However, Cl-rich seawater can damage the passive Cr_2O_3 film formed in the 15-5 PH region. The average pitting depth of NAB and 15-5 PH was measured to be 0.25 and 1.4 μm , respectively, indicating that NAB has higher pitting resistance than 15-5 PH (Figure 5.17f).

A copper/nickel bimetallic structure was fabricated via L-DED using a GRCo-84 copper alloy and Inconel 718 to enhance the thermophysical performance of aerospace components (Figure 5.18a) (Oniuke et al. 2018). A gradual transition between Inconel 718 and GRCo-84 at their diffused interface was achieved using the compositional gradation technique (Figure 5.18b,c). Columnar grain structures were formed at the interfaces with the accumulation of Cr_2Nb precipitates along the grain boundaries and the substrate–deposit interface. The average thermal

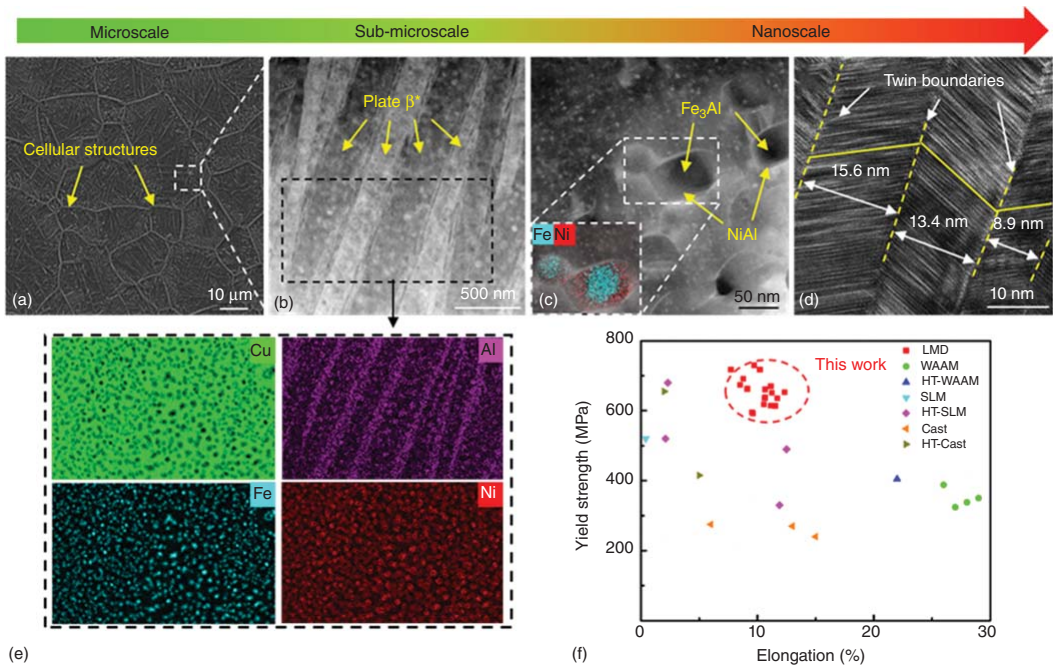


Figure 5.16 Hierarchical microstructure of a printed Cu-9Al-5Fe-5Ni alloy, including (a) cellular structures, (b) the plate martensite β^* phase, (c) Fe₃Al and NiAl nanoprecipitates, and (d) nanotwins at the boundaries of the β^* plates. (e) Elemental distribution in the rectangular region indicated in image (b). (f) Comparison of the mechanical properties of nickel–aluminum–bronze alloys fabricated by L-DED and other processes. Source: Li et al. (2021)/reproduced with permission from Elsevier.

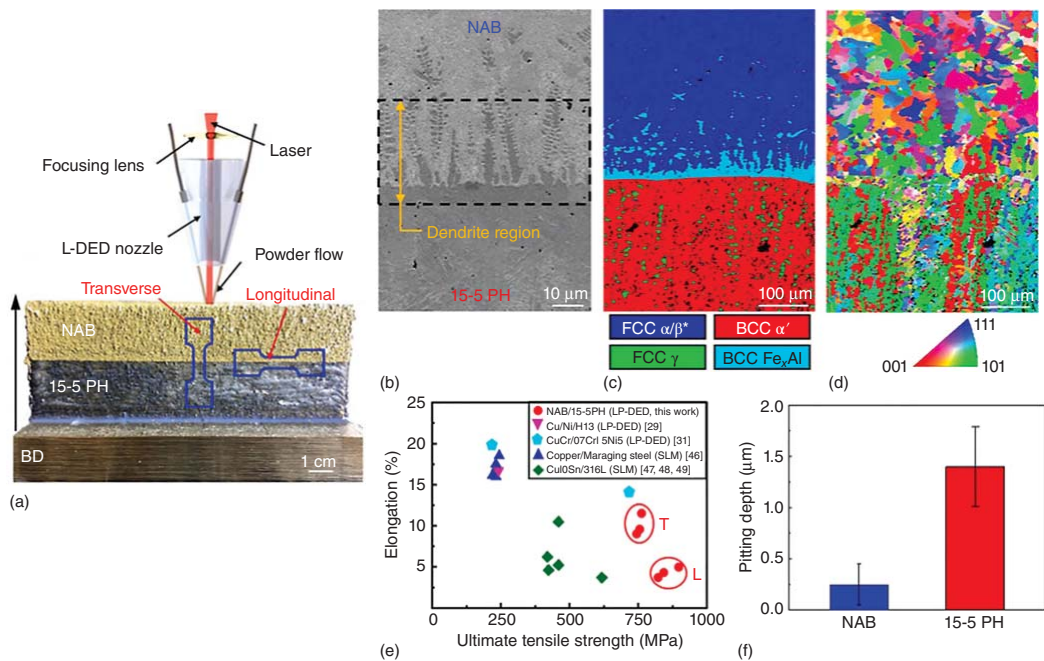


Figure 5.17 Multi-material samples manufactured by L-DED. (a) Schematic of the L-DED process, (b) SEM image, (c) phase distribution, and (d) IPF map of an NAB/15-5 PH multi-material sample. (e) Comparison of the mechanical properties of copper/steel multi-materials fabricated by AM. (f) Comparison of the pitting depths of NAB and 15-5 PH. Source: Li et al. (2022)/reproduced with permission from Elsevier.

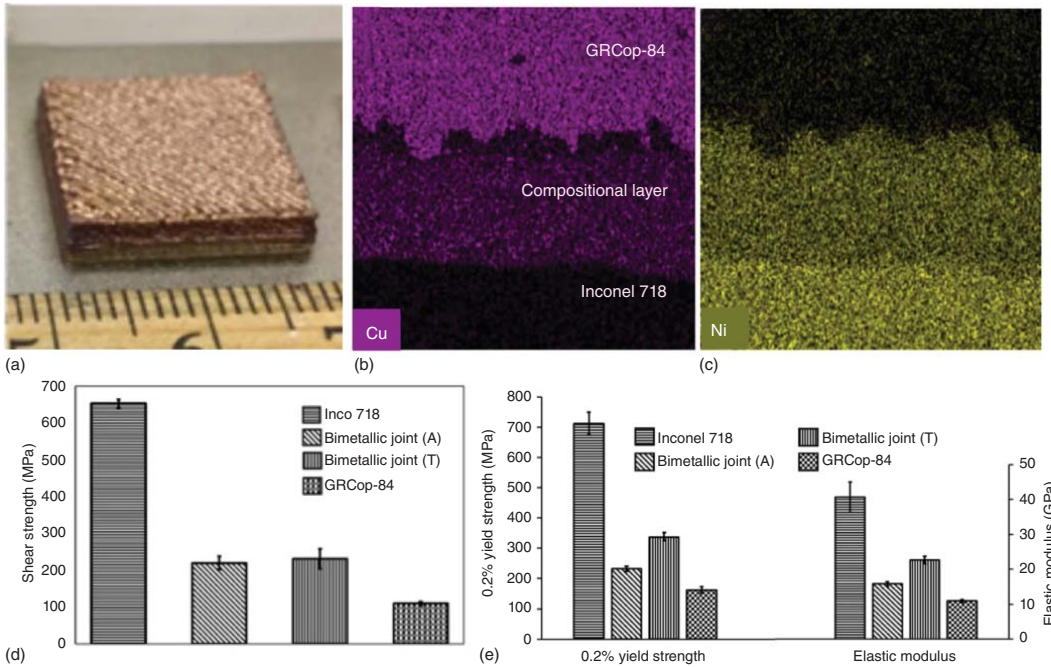


Figure 5.18 (a) Bimetallic Cu–Ni structure fabricated via L-DED; the elemental distribution of (b) Cu and (c) Ni at the Cu–Ni interface indicates the gradual transition of composition. Source: Oniuke et al. (2018)/reproduced with permission from ELSEVIER. (d) Shear strength and (e) compression properties of the bimetallic structure before and after one thermal cycle. Source: Reproduced from Oniuke and Bandyopadhyay (2019)/with permission from Elsevier.

diffusivity of the bimetallic structure improved by 250% from 3.20 to 11.33 mm²/s for temperatures ranging from 50 to 300 °C. The thermal conductivity of the bimetallic structures increased by almost 300% compared to that of Inconel 718. A peak hardness value of 2.95 GPa was obtained in the HAZ.

The influence of thermal cycling on the shear and compressive strength of a bimetallic GRCo-84/Inconel 718 joint was evaluated (Onuik and Bandyopadhyay 2019). The shear strength of the bimetallic joint before and after thermal cycling was measured to be 220 and 231 MPa, respectively (Figure 5.18d). After thermal cycling, no crack was observed at the interface of the bimetallic joint, indicating that it did not undergo thermal degradation. On the other hand, the compressive yield strength of the Inconel 718 joint before and after thermal cycling was 232 and 337 MPa, respectively (Figure 5.18e), and such an improvement was attributed to the precipitation of Cr₂Nb particles in the copper matrix and the strengthening effect of gamma phases in Inconel 718.

Pure copper processed by L-DED exhibits a graded microstructure with coarse equiaxed grains of 10–20 μm, Cu₂O macro-precipitates of 200 nm, and Cu₂O nano-precipitates of 2–3 nm due to multiple thermal cycles (Zhong et al. 2018), during which oxygen is solubilized in the melting pool. In the primary thermal cycle, some oxygen precipitates and forms macro-sized Cu₂O, while nano-sized Cu₂O is formed in the later thermal cycles when the remaining oxygen precipitates. The nano-sized precipitates provide better precipitation hardening effects and contribute to the greater hardness of the printed parts.

5.7.4.3 High-Entropy Alloys

L-DED can not only employ pre-alloyed HEA powders but also simultaneously deliver different pure metal powders from multiple hoppers to print HEA products through *in situ* alloying. Elemental powders are delivered, melted, and deposited onto a substrate, forming an alloy product. Homogeneous distribution of the elements can be obtained through optimizing the process parameters and remelting via repetitive scanning, thereby enhancing the flexibility of the composition design of HEAs for materials development. The printing of HEA products through L-DED for powders such as AlCoCrFeNi, AlCrCuFeNi, AlCoFeNiCu, CoCrFeMnNi, and TiZrNbTa has been validated. Such products showed a yield strength of 194–518 MPa, an ultimate tensile strength of 535–660 MPa, an elongation of 19.8–55%, and a microhardness of 195–860 HV (Han et al. 2020).

L-DED exhibits great potential to develop functionally graded HEA parts through the *in situ* alloying of elemental powders. A compositionally graded Al_xCrCuFeNi₂ (0 ≤ x ≤ 1.5) sample was fabricated through L-DED to investigate the influence of systematic compositional changes on its microstructural evolution, mechanical properties, and magnetic properties (Figure 5.19a) (Borkar et al. 2016).

With an increase in aluminum content from 0 to 1.5 (mole fraction), the printed Al_xCrCuFeNi₂ HEA products exhibited a transition in their crystal structure from overwhelmingly FCC (98%) and minimally BCC (2%) (Figure 5.19b) to predominantly BCC (80%) and substantially FCC (20%) (Figure 5.19c). The volume fraction of the ordered L1₂ FCC phase also increased and then decreased.

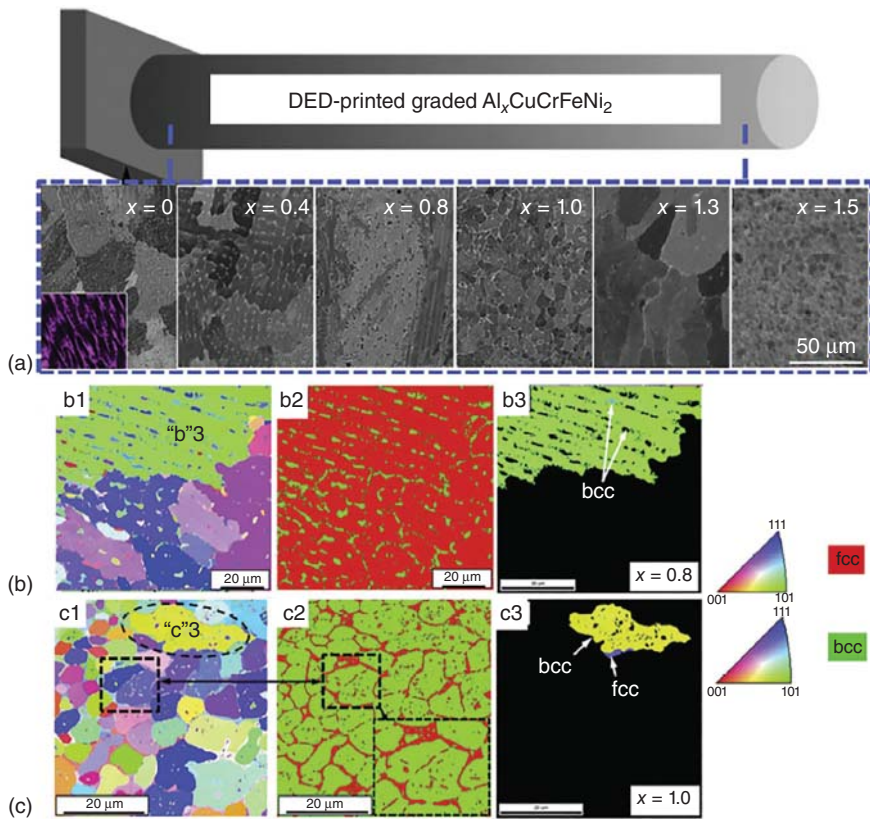


Figure 5.19 Microstructure of compositionally graded Al_xCuCrFeNi₂ HEA products printed by L-DED. (a) Morphology and (b) EBSD results for Al_{0.8}CuCrFeNi₂: (b1) various orientations and the inverse pole figure map, (b2) phase map demarking FCC and BCC regions, and (b3) the inverse pole figure map of a selected grain in (b1). (c) EBSD results for AlCuCrFeNi₂: (c1) various orientations and the inverse pole figure map, (c2) phase map demarking FCC and BCC regions, and (c3) the inverse pole figure map of a selected grain in (c1). Source: Borkar et al. (2016)/reproduced with permission from ELSEVIER.

These phenomena are attributed to the addition of aluminum distorting the FCC lattice, thereby inducing the transition from a close-packed FCC phase to a more loosely packed BCC phase.

5.8 Summary

L-DED delivers feedstock and laser energy simultaneously on a freeform surface in a layer-by-layer manner. Both emerging and established manufacturing corporations have developed many commercial L-DED machines. The modular design of L-DED machines provides flexibility in selecting the printing dimension, laser source, powder feeder, printing chamber, deposition nozzle, etc., to meet practical requirements.

Available materials include various titanium and its alloys, nickel alloys, iron alloys, aluminum alloys, copper alloys, and HEAs.

L-DED has been widely employed to fabricate original parts, add new features to existing parts, and repair damaged parts for aerospace, automotive, biomedical, and maritime applications. Several vital aspects of L-DED, including material development, printing efficiency and accuracy, online monitoring and defect inspection, process mechanism, and standardization and certification, have gained increasing interest from both academia and industries. These aspects inspired the realization of the full potential of L-DED and promoted its market uptake.

Repairing/adding new features to an existing part is a distinctive advantage of L-DED that holds a promising future. Repairing high-value or unique parts through L-DED can significantly reduce costs and lead time. Adding new features such as composite coatings to extend wear resistance or provide biocompatibility enhances the product performance.

Multi-material printing can endow a single product with a combination of multiple desirable properties by depositing different materials at designated locations, which improves its thermal conduction, corrosion resistance, wear resistance, etc. Material development is also an attractive aspect of multi-material printing because its versatile composition control permits the administration of high-throughput experiments and the rapid screening of target materials. Nevertheless, the performance of multi-material delivery devices, the interactions between multi-materials and laser sources, and multi-material printing strategies require further investigation.

Hybrid manufacturing also displays an increasing propensity to be incorporated into L-DED as printing resolutions are typically low due to the large melt pool size. Post-machining modules are expected to be integrated with traditional L-DED machines to manufacture products with the required dimensions directly. Such manufacturing strategies that involve both additive and subtractive manufacturing techniques must be optimized to balance the precision and processing efficiency.

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6

Metal Binder Jetting

In metal binder jetting (MBJ), a liquid binder is selectively deposited onto layers of metal powder to bond powder particles and produce green parts. Subsequently, a sintering process is often conducted to densify such green parts. Among metal powder-based additive manufacturing (AM) techniques, MBJ exhibits excellent potential for the high-speed and low-cost fabrication of complex structures. This chapter discusses the history, fundamentals, printing process, raw materials, and equipment of the MBJ technique and the microstructures and mechanical properties of MBJ-printed parts.

6.1 History

Binder jetting, originally termed “three-dimensional printing”, was invented at the Massachusetts Institute of Technology. In this method, a glycerin/water binder is jetted onto gypsum-type powder layers through thermal bubble inkjet printheads (Sachs et al. 1992). The technique was first commercialized by Z Corporation, which also introduced full-color printing capabilities to its machine models (Ian Gibson 2015).

In 1996, Extrude Hone licensed the patents from the Massachusetts Institute of Technology to fabricate metal parts, after which the company launched its first binder jetting printer system, ProMetal RTS-300. In 2005, ExOne, a spin-off of Extrude Hone, focused on printing stainless steel parts infiltrated with bronze (Wohlers 2014). One of the popular applications for the MBJ technique is to manufacture sand molds and cores for the casting industry. The interest in MBJ has grown recently, along with increased research and development of large-size part printing and high-throughput production.

6.2 Fundamentals

An illustration of the MBJ process is presented in Figure 6.1 (Mostafaei et al. 2021b). As shown in Figure 6.1a, a layer of powder is first spread on the build bed and compacted by a rotating roller. Next, a liquid binder composed of polymers in a solvent

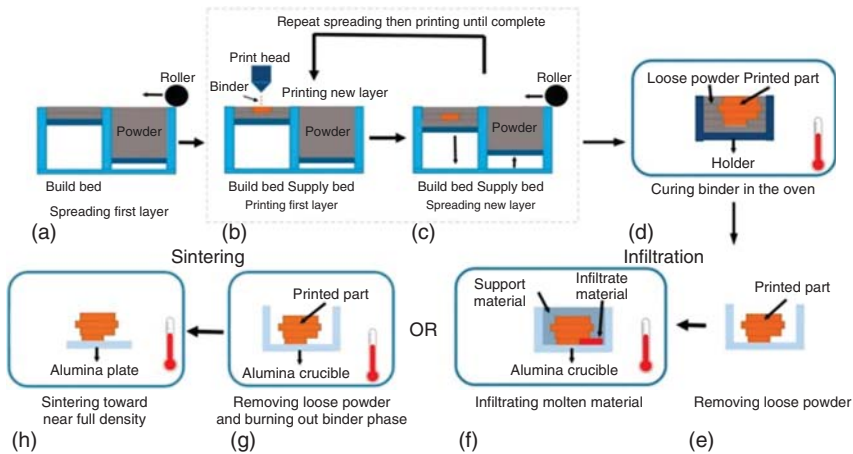


Figure 6.1 Schematic illustration of the MBJ process. (a) Preparing a powder layer on the build bed, (b) printing the binder on the powder layer through a printhead, (c) repeating the powder spreading and printing steps, (d) curing the binder, (e) depowdering the cured green parts, (f) infiltrating, and (g, h) sintering. Source: Mostafaei et al. (2021b)/reproduced with permission from Elsevier.

or aqueous solution is jetted from the printhead onto the powder layer to create a two-dimensional cross-section of the printed part (Figure 6.1b). An electrical heater or ultraviolet-band curing lamp that is installed in the powder spreading system traverses across the powder bed to partially dry or cure the layer at a uniform temperature and prepare it for the spreading of the next layer. Subsequently, the build bed moves downward by the thickness of a single layer (commonly in the range of 15–300 μm), and the powder-spreading and printing steps are repeated until the part is complete (Figure 6.1c).

Once the printing step is completed, a curing step, in which the printed part will be removed from the printer and heated until the binder is adequately dry, will be carried out to infuse the former with “green” strength (Figure 6.1d). Such printed parts have not undergone densification through infiltration or sintering. During a typical curing process, the entire build bed, which contains the loose powder and printed part, is placed in an oven and heated at 180–200 $^{\circ}\text{C}$.

After curing, the green parts are depowdered in a densification furnace to remove loose powder via manual brushing (Figure 6.1e). The relative density of the green parts ranges from 50% to 60% after the depowdering process. Further densification of the green parts can be achieved through sintering or by infiltrating them with another molten material (Figure 6.1f–h).

MBJ is a less prominent AM technique than powder bed fusion (PBF) and directed energy deposition (DED). The advantages of the MBJ process are:

- MBJ is theoretically compatible with any powder material and boasts the widest range of material selection among all the metal powder-based AM processes. In particular, certain difficult-to-print materials (such as refractory pure metals and alloys) can be effectively printed through MBJ without encountering processing issues present in PBF.

- The MBJ process is conducted at room temperature and in an open atmosphere, thereby eliminating the residual stress, element segregation, and phase transformation, which are all common issues in PBF processes.
- No support structures are required for any part fabricated by MBJ because it is almost free of residual stress. In contrast, support structures are often employed for the overhanging features of PBF-printed parts.
- The build volume of MBJ machines is generally larger than that of other metal powder-bed AM processes.
- MBJ displays excellent high-speed and low-cost manufacturing capabilities and renders the loose powders highly recyclable.

The main disadvantages of MBJ are as follows:

- MBJ is a multistep process that requires post-processing steps (curing and densification). The development of post-processing strategies is still necessary for most MBJ powder materials.
- MBJ-printed green parts often exhibit low relative densities, which may result in significant shrinkage and geometric distortion during their densification.
- MBJ-printed parts exhibit low resolution and high surface roughness.

6.3 Printing Process

The binder plays a critical role in the MBJ process. A liquid binder is jetted onto the powder bed and infiltrates the gaps between the powder particles in each printed layer to create predefined two-dimensional patterns. The viscosity and surface tension of the binder are two essential factors when the binder is jetted through the printhead since the binder should not solidify inside the printhead. Aside from effectively bonding the powder particles, the binder must remain stable at high temperatures of up to several hundred degree Celsius during the curing process. Additionally, the binder should display good wettability with the powder particles and generate minimal residue after pyrolysis. The binder classes have been categorized, namely, acid-based binder, hydration-based binder, metal salt-based binder, inorganic binder, organic binder, phase-changed binder, solvent-based binder, and thermal-cured binder (Utela et al. 2010).

The interactions between the binder and powder particles determine the geometric accuracy, strength, and surface quality of the printed parts before and after post-processing (Bai et al. 2019). A series of infiltration kinetics occur when the binder is jetted onto the powder bed; such infiltration kinetics are mainly influenced by the characteristics of the binder droplets and the powder bed. Characteristics of the binder droplets include their volume, initial velocity, viscosity, and spreading and wetting behaviors, as well as the duration for them to penetrate the powder bed. Meanwhile, the roughness of the powder bed can affect the spreading, wetting, and penetrative behaviors of the binder droplets.

The liquid binder droplets, at the size of a few dozen microns, typically collide with the top surface of the powder particles at a substantial impact velocity (Figure 6.2a), resulting in their spreading across the powder bed and forming liquid networks

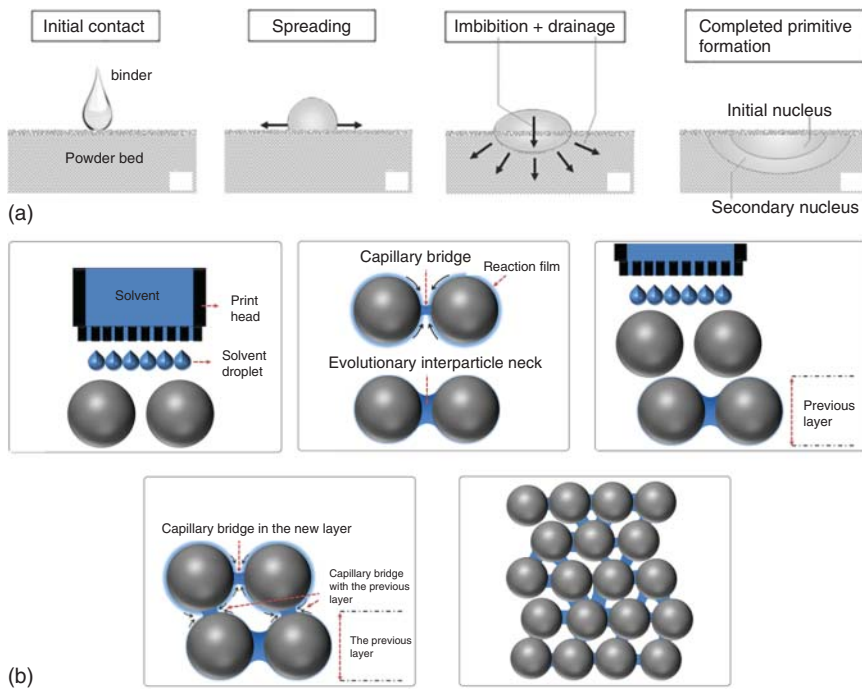


Figure 6.2 Schematic illustration of the binder–powder interactions in MBJ. (a) Interaction between a binder droplet and the powder bed. Source: Reproduced from Bai et al. (2019)/with permission from American Society of Mechanical Engineers. (b) Interaction between binder droplets and powder particles. Source: Salehi et al. (2019a)/reproduced with permission from Elsevier.

that bond adjacent powder particles. Subsequently, the binder droplets penetrate the loose powder particles beneath the top surface under the capillary force effect (Figure 6.2b).

Figure 6.3 presents the different granule formation mechanisms of a binder droplet impacting the powder bed, which include tunneling, spreading, and cratering (Emady et al. 2011). The tunneling mechanism is mainly restricted to fine and cohesive particles. A binder droplet attracts loosely aggregated particles as it penetrates the powder bed and forms spherical granules. Such granules may display protrusions due to the incomplete penetration of the binder droplet.

Spreading and cratering mechanisms are dominant in the case of coarse and free-flowing powder particles. When a slow-moving binder droplet impacts a dense powder bed, the droplet spreads across the surface of powder particles and forms a flat disk (Figure 6.3b). On the contrary, a binder droplet moving at a high velocity can create a crater in the powder bed upon collision before spreading upward along the walls of the crater, gathering powder particles, and finally retracting (Figure 6.3c).

The scanning strategies employed in MBJ directly influence the binder-powder interactions and the resolution of the printed parts. These strategies include vector scanning, raster scanning, and vector tracing with rasterization. In the vector scanning strategy (Figure 6.4a), the binder droplets create a contour and move inward to progressively trace smaller contours until a complete powder layer is printed.

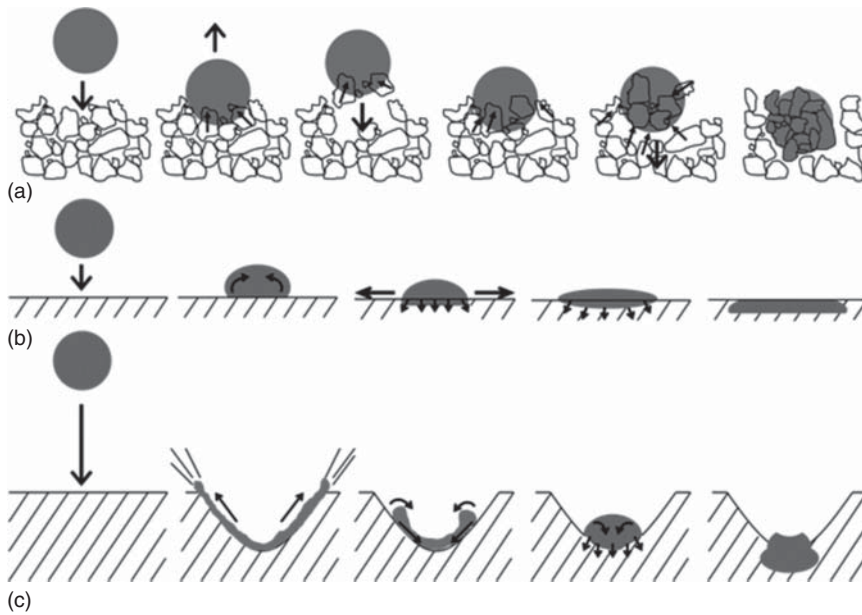


Figure 6.3 Schematic illustration of different granule formation mechanisms. (a) Tunneling, (b) spreading, and (c) cratering. Source: Emady et al. (2011)/reproduced with permission from Elsevier.

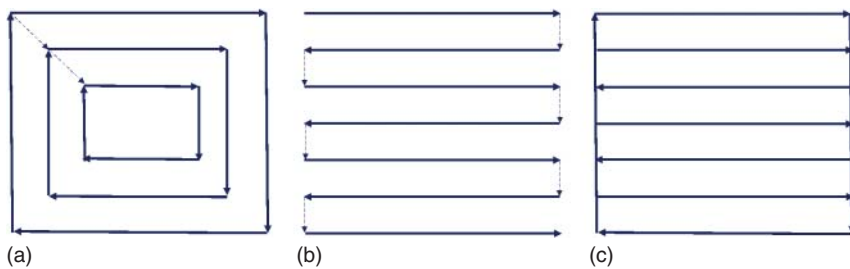


Figure 6.4 Schematic illustration of the main scanning strategies in MBI. (a) Vector scanning, (b) raster scanning, and (c) vector tracing with rasterization.

This strategy produces the most geometrically accurate parts. However, utilizing only a single nozzle in the printhead increases the printing time (Baker 1997).

The raster scanning strategy (Figure 6.4b) entails the printhead first jetting binder droplets along the x direction. Subsequently, the printhead moves along the y direction and commences to scan a new line along the x direction (Miyanaji et al. 2018). While this strategy may create an undesirable stair-stepping appearance between adjacent lines, the utilization of multiple nozzles results in a higher printing speed. Vector tracing with rasterization uses the same scanning pathway as the vector scanning strategy (Figure 6.4c). The printing speed can be increased by employing all the nozzles in the printhead during the raster scanning process, which also ensures smoother edges on the surfaces of the parts (Baker 1997).

In MBJ, the layer thickness is typically in the range of 15–300 μm , and is determined by the printing resolution and the size of the powder particles. As a rule of thumb, a layer thickness approximately three times the average powder particle size should be implemented to ensure sufficient space for the rearrangement of the powder particles, beyond which an increase in layer thickness may reduce the density of the powder bed. Generally, a highly dense powder bed corresponds to a highly dense green part, which undergoes less shrinkage during the sintering process.

The powder spreading speed, which is comprised of the recoating speed, oscillator speed, roller speed, and roller traverse speed, determines the overall printing efficiency. Specifically, the recoating speed refers to the traveling speed of the recoater, which spreads powder onto the powder bed in the horizontal direction. The oscillator speed is the frequency at which the dispensing mechanism oscillates. The roller speed refers to the rotational speed of the roller, and the roller traverse speed is the speed at which the rotating roller moves across the powder bed. Coordinating these parameters is necessary to ensure the high quality of the printed green parts.

The saturation level of the binder depends on the capacity of the printhead system. The volume of droplets dispensed by printheads can be adjusted, which in turn affects the minimum saturation level and results in droplet overlapping (Miyanaji et al. 2016). The theoretical binder saturation S (%) can be estimated by

$$S = \frac{1000V}{\left(1 - \frac{R}{100}\right)XYZ}, \quad (6.1)$$

where V is the average volume of each binder droplet (pL), R is the powder packing rate (%), X and Y are the spacing between the jetted binder droplets along the x and y directions (μm), respectively, and Z is the layer thickness (μm). A low binder saturation can cause delamination of the printed layers and result in high porosity in the printed parts after sintering. Conversely, excessively high binder saturation may lead to loose powder particles adhering to the surfaces of the green parts and the roller, thereby contributing to high surface roughness and dimensional inaccuracies of the green parts and resulting in inhomogeneous powder spreading, respectively. High saturation levels may also increase the printing time. Therefore, optimizing the saturation level is vital for improving the printing efficiency, enhancing the strength of the green parts, and minimizing the cost.

The level of binder saturation can be influenced by the layer thickness and powder characteristics. For example, if the layer thickness value is smaller than the average size of the powder particles, the amount of binder administered may be excessive. The surplus binder may spill to the sides and produce large parts with a rough surface. On the contrary, a large layer thickness provides sufficient space to accommodate the binder and reduces binder spillage. The porosity of the powder bed and the contact angle between it and the binder jet are the two main factors influencing binder infiltration; an increase in the porosity and contact angle can reduce the infiltration depth and area of contact between the binder and the powder bed, respectively.

After jetting the binder droplets onto the powder bed, the powder bed surface is exposed to the heat emitted from a resistive heater for initial curing. This process

is also known as drying. The drying duration is affected by the binder saturation level, binder composition, layer thickness, wettability between the powder and the binder, and powder bed characteristics (e.g. thermal conductivity, surface area, permeability, and packing density). Excessively high drying temperatures or an extended drying duration may lead to the slice cracking of parts during the subsequent powder spreading process, which is attributed to the shear forces produced by the roller and the fragility of the dried layer. During the drying stage, excessive binder is utilized to cleanse the printhead to prevent blockage within its nozzles.

The printed green parts must undergo curing, depowdering, measurement of their green strength, debinding, and infiltration or sintering. A hot isostatic pressing (HIP) step can also be optionally performed.

Curing is conducted to increase the strength of the printed parts. Typically, the powder bed and printed parts are both cured in the same oven to remove the binder within the latter. The curing temperature and duration are critical parameters determined by the binder material, part geometry, volume of the powder bed, etc. The cured green parts should possess sufficient mechanical strength to withstand the subsequent depowdering process, during which loose powder particles are removed manually through brushing, air jetting, vibrating, or vacuuming. In particular, wet depowdering methods (e.g. ultrasonic techniques, microwave-induced boiling, and CO₂ bubble generation in soda water) can be employed when the binder is insoluble within the corresponding fluid.

The green strength is critical to preserving the delicate features and geometries of the printed parts during the depowdering process, during which a green part of ultralow strength may succumb to breakage. However, a green part exhibiting exceptional strength likely contains an excessive amount of binder, which corresponds to a rough surface. Therefore, the strength of such green parts should be evaluated and prioritized during process optimization.

Before the densification process, the binder in the cured green parts must undergo a burnout step, i.e. debinding, because it may impede the sintering and infiltration processes. Typically, the burnout step is performed in the same furnace designated for sintering or infiltration, and the burnout temperature can be determined through differential thermal analysis of the binder. Unfortunately, some oxygen and carbon residue may remain even after the binder decomposes or becomes gaseous (Yan et al. 1993). The oxygen residue may oxidize the surface of the printed parts. In contrast, the carbon residue may form carbides when the burnout procedure is conducted at high temperatures, thereby degrading the mechanical properties of MBJ-printed metal parts sensitive to carbon or oxygen (Miyanaaji et al. 2016).

Infiltration is an alternative densification method that utilizes an alloy material to improve the relative density of the printed green parts. The infiltrant material should possess a lower melting temperature than the powder material of the green parts. The dominant mechanism underlying the infiltration process is the capillary action involving the liquid infiltrant and the interspaces of the powder particles. Infiltration can significantly reduce the porosity of the printed green parts and improve their mechanical properties (Do et al. 2015). Note that optimizing the

saturation of the infiltrant is critical to achieving high densification of the green parts. If the amount of infiltrant administered exceeds its saturation level, the dimensional accuracy of the printed parts may be compromised. On the other hand, utilizing an insufficient amount of infiltrant results in weak bonding between the powder particles.

Sintering is a basic densification method for processing binder-jetted green parts. The sintering kinetics depend on the chemistry, surface activity, morphology, and size distribution of the powder particles and the sintering atmosphere. Metallic bonds are formed during the sintering process. As a result, the green parts experience shrinkage during sintering, and pores formed during the printing process are filled. Two categories of sintering mechanisms exist, namely, densifying and non-densifying sintering mechanisms.

At lower temperatures, the sintering process is dominated by non-densifying sintering mechanisms, which include diffusion on the surface of the powder particles and vapor transport. Such mechanisms are coupled with particle coarsening and negligible interparticle neck growth. The densifying mechanisms begin to dominate the process as the temperature increases. For metals, the primary densifying mechanisms are grain boundary diffusion and lattice diffusion between the powder particles (Rahaman 2010).

Figure 6.5 shows the three stages of the sintering process (German 2010). The initial stage occurs at a low temperature, and it is dominated by non-densifying sintering mechanisms. No significant densification or powder particle movement occurs at this stage. Notably, the average size of the interparticle necks is less than one third of the average particle size. Due to voids in the powder bed, pores are distributed across the entire part, and its relative density is over 30% lower than its theoretical density.

The intermediate stage occurs when the temperature increases to a certain material-dependent threshold. At this stage, the sintering mechanisms are predominantly grain boundary diffusion and lattice diffusion between the powder particles, which promote interparticle neck growth and the mass movement of powder particles. As the sintering process proceeds, the interparticle necks reach approximately half the average particle size. Additionally, large pores within the part merge to form tubular pores and gradually eliminate the fine pores. In the first two stages, the pores on the surface of the part remain open, allowing gases within it to escape.

At the final stage, the sintering temperature range is similar to the one in the intermediate stage, and the maximum densification effect can be achieved with optimized sintering conditions. Critical aspects of the MBJ sintering process include the heating and cooling rates, the sintering temperature, and the holding time. Note that it is highly challenging to attain the near-full density of the green part even after sintering.

All MBJ-printed green parts are highly porous before sintering. In such parts, the powder particles are closely packed together in the near absence of external forces, and their solid volume fraction is typically below 60%. The low density of the green parts may result in high shrinkage during their densification, and such shrinkage should be considered during the stages of process optimization and part design. Live Sinter, a software solution developed by Desktop Metal, can

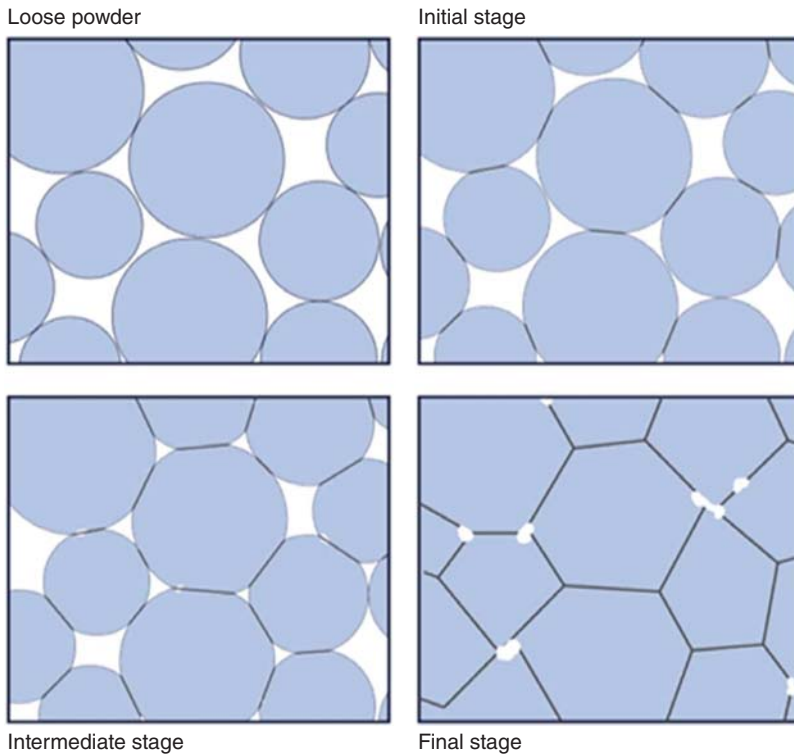


Figure 6.5 Illustration of three sintering stages, revealing the details in the evolution of the pore structure. Source: German (2010)/reproduced with permission from Elsevier.

predict the shrinkage and distortion that green parts undergo during the sintering process. Such discrepancies can be automatically compensated, thereby granting the printed parts their original design geometries after sintering.

6.4 Raw Materials

Different binders are currently being developed and employed for MBJ, including polymeric binders, metal nanoparticle suspensions, metal oxide precursors, metal salts, and metal-organic decomposition (MOD) inks. Ethylene glycol-based binders are the most widely utilized binders because of their excellent solubility in water, high cost effectiveness, long-lasting effects, and good burnout properties. However, selecting an appropriate binder ensures that the printed parts exhibit sufficient mechanical strength. Additionally, the pyrolysis of polymer binders during post-sintering may produce carbon residue, which may degrade the purity and the mechanical, optical, electrical, and thermal properties of the printed parts.

Presently, the types of metal powder materials researched for MBJ applications are fewer than those for PBF and DED. Table 6.1 provides a summary of the most studied powder materials for MBJ. There are also emerging metal materials under development for MBJ, such as magnesium alloys and aluminum alloys.

Table 6.1 Summary of the most investigated powder materials for MBJ.

Materials	Commercial equivalents
Iron-based alloys	316L, 17-4, 304L, 420, Fe–Mn, Fe–Mn–Ca, Fe–Si, H13, D2
Nickel-based alloys	718, 625
Titanium-based alloys	Ti–6Al–4V
Cobalt-based alloys	Co–Cr–Mn
Pure metals	Cu, W, Fe, commercial pure Ti
Magnetic alloys	Ni–Mn–Ga, Nd–Fe–B, Fe–6Si

Powder characteristics such as the morphology, size, and size distribution of the particles are also critical factors affecting the efficacy of the MBJ process. Powder morphology influences the spreading of powder particles on the powder bed, as well as the green density and the sintered density of the printed parts. Spherical powder morphology is preferable in MBJ because of the low internal friction and good flowability it offers. In contrast, an irregular-shaped powder morphology corresponds to a smaller interparticle contact area, thereby giving rise to larger pores in the printed parts.

The flowability and sinterability of a powder, which are dominant properties in the MBJ process and its post-processing, respectively, are significantly affected by the size distribution of its powder particles. Based on machine specifications, the print-head resolution and the average powder particle size may range from sub-microns to 150 μm . Finer powders generally demonstrate lower flowability due to the more pronounced effects of particle interactions (e.g. van der Waals, electrostatic, and capillary interactions). Compared to fine powders, the flowability of coarse powders is less dependent on interparticle forces because of the large inertia and small contact areas of each powder particle.

The powder particle size distinctly impacts the powder bed and green parts. For example, the spreading performance of Inconel 718 powder ($<20\ \mu\text{m}$) was shown to be inferior to that of powders with a larger powder particle size ($<53\ \mu\text{m}$) as a result of more powder agglomeration, creating a large number of pores in the powder bed and eventually reducing the density of the green parts (Turker et al. 2008). However, fine powder particles typically correspond to high powder sinterability, which can be attributed to their higher surface-to-volume ratio and energy state. As a result, fine powder particles are sintered within a shorter time than their larger counterparts, resulting in fast densification.

To tackle the aforementioned issues of employing fine powders, ExOne (USA) has developed a Triple ACT system to improve the dispensing, spreading, and compacting of fine powders ($\leq 10\ \mu\text{m}$) to print high-quality metal parts displaying high surface quality, dimensional accuracy, and sinterability.

The morphology and size distribution of powder particles can influence the pore size distribution and homogeneity of the powder bed density, which further impacts binder penetration. Powder particles prepared by water atomization or ball

milling typically exhibit irregular shapes and may cause heterogeneous powder spreading, which introduces difficulties in attaining complete binder penetration. Small powder particles may also create macropores within the powder bed due to particle agglomeration, thereby increasing the drop penetration time.

6.5 Equipment

The leading companies in the development of commercial binder jetting equipment are ExOne (USA), Voxeljet (Germany), 3D Systems (USA), and Digital Metal (Sweden). Their equipment is capable of printing metals, ceramics, and waxes. Additional MBJ systems have been proposed by Desktop Metal (USA), GE Additive (USA), 3DEO (USA), Hewlett–Packard (HP) (USA), and Long Yuan (China). Among these companies, ExOne boasts the greatest variety of machines that can print using a wide range of metal powders, including stainless steel 316, 420, 17-4 PH, Inconel 625, Inconel 718, pure iron, iron–chrome–aluminum, chromite, cobalt–chrome, and tungsten powders.

GE Additive first announced its venture into the domain of binder jetting in 2017, with the debut of the prototype system H1. The company has since been developing a second generation of the H1 system, which is expected to be commercially available. A summary of standard commercialized equipment for MBJ is listed in Table 6.2.

A significant difference in the equipment of MBJ and PBF is the printhead, which is a core component of the former. Figure 6.6 shows the different types of printheads used to generate liquid binder drops, namely, drop-on-demand (DoD) and continuous-jet (CJ) printheads (Salehi et al. 2018).

Thermal inkjet and piezoelectric printheads are the two types of standard DoD printheads that can produce individual drops on demand. In thermal inkjet printheads, the heater vaporizes a portion of the liquid binder. The subsequent volume expansion of the vaporized binder results in the liquid binder being ejected through the nozzle (Kwon and Kim 2007). Meanwhile, piezoelectric printheads can be utilized to promote ink development because their rheological properties constitute the only requirement for producing a reliable flow of ejected ink.

In CJ printheads, the binder droplets are continuously produced at higher print rates than droplets produced by DoD printheads. In specific areas on the powder bed where the binder does not have to be applied, the inductively chargeable binder droplets can be deflected into a gutter. Compared to DoD printheads, CJ printheads correspond to a slow traverse speed and decent size control over overlapping printed tracks.

HP thermal inkjet printheads, which are installed in HP Metal Jet printers, can facilitate the precise placement of the binder on the powder bed. As shown in Figure 6.7a, each printhead comprises an electrical connector, two independent supply ports for binders, two pressure regulators, and nozzles. There are 5280 nozzles on the top surface of each pressure regulator, and each nozzle is spaced 1/1200 in. from one another. The binder is initially fed into the supply ports and subsequently pumped out by the pressure regulators. Multiple printbars are utilized

Table 6.2 Summary of standard commercialized equipment for MBJ.

Company	Equipment	Build volume (mm)	Throughput (cc/h)	Print resolution	Layer thickness (μm)	Size (<i>D</i> × <i>W</i> × <i>H</i>) (mm)	Materials and binders
ExOne (USA)	Innovent+	160 × 65 × 65	166	30 μm voxels	30–200	1203 × 1016 × 1434	Materials: 17-4 PH, 304L, 316L, M2 tool steel, Co–Cr, copper, H13 tool steel, Inconel 625, titanium, tungsten. Binder systems: Aqueous, solvent, phenolic
	X1 25PRO	400 × 250 × 250	3600	>30 μm voxels	30–200	2300 × 1800 × 2300	
	M-Flex	400 × 250 × 250	1600	>50 μm voxels	50–200	1675 × 1400 × 1855	
	X1 160Pro	800 × 500 × 400	>10 000	—	30–200	—	
Digital Metal (Sweden)	DM P2500	170 × 150 × 55; 203 × 180 × 69	60; 100	35 μm	—	2900 × 1000 × 1700	316L, 17-4 PH, Ti–6Al–4 V, Ni 625, Ni 247
Desktop Metal (USA)	Shop System™	350 × 222 × 200	700	1600 dpi	40–100	1994 × 762 × 1626	Materials: 17-4 PH
	Production System	490 × 380 × 260	12 000	1200 dpi	—	1900 × 5000 × 1900	Binder systems: Waxes and polymers
HP (USA)	HP Metal Jet	430 × 320 × 200	—	1200 dpi	50–100	—	Materials: 316L. Binder systems: Polymers

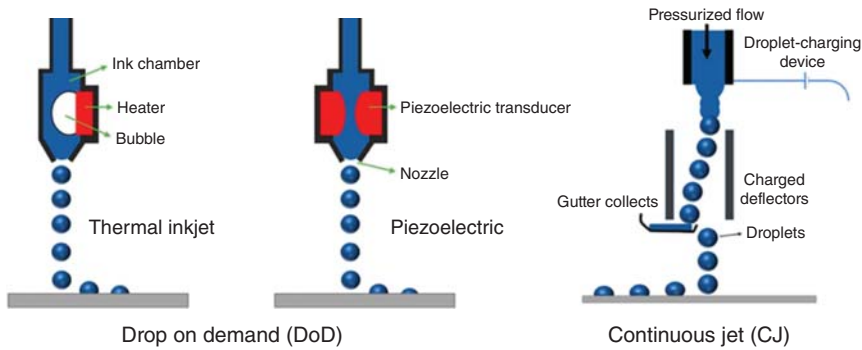


Figure 6.6 Schematic illustration of drop-on-demand and continuous-jet printheads. Source: Salehi et al. (2018)/reproduced with permission from Materials Research Forum.

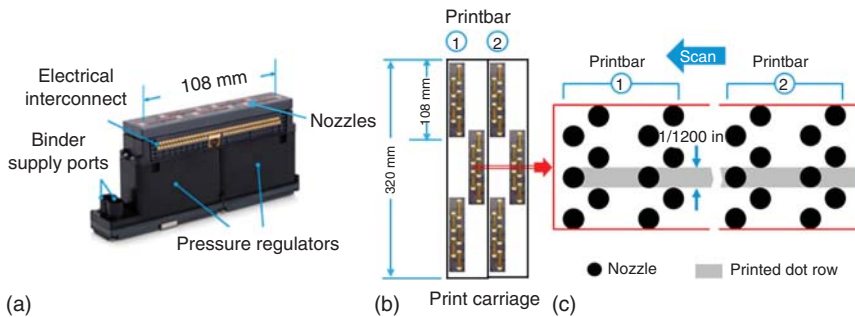


Figure 6.7 HP thermal inkjet printhead in HP Metal Jet printers. (a) Image of the printhead, (b) a print carriage containing two printbars, and (c) schematic illustration of each printbar. Source: Courtesy of HP.

in each printer cartridge to boost productivity. As shown in Figure 6.7b, each printbar contains three printheads arranged in the form of an isosceles triangle and can create a 320 mm-wide print swath. Two printbars (marked as 1 and 2) in the print carriage are aligned to ensure that the nozzles (represented by black dots) can operate along the same line to print a dotted row (indicated by gray lines) with 1/1200 in. between the dots (Figure 6.7c). Consequently, up to four different nozzles can function simultaneously within the same 1200 dpi grid point.

6.6 Microstructure and Mechanical Properties

MBJ is theoretically applicable to printing parts from a wide range of materials because of its inherent aspect of forming parts without material fusion. Compared to laser-based AM (PBF and DED), MBJ can print thermally conductive, hard-to-weld, and refractory materials. Notably, densification of printed parts remains a top priority of the MBJ printing process and the post-treatment of green parts.

Table 6.3 Summary of the tensile properties of MBJ-printed metallic materials after densification.

Material	Relative density (%)	σ_y (MPa)	σ_{UTS} (MPa)	ϵ (%)
Iron	91.3	30.6	—	—
316L	95–98	180–224	494–582	51–61.9
304L	97	205	579	60
17-4 PH	98	730–1034	900–1317	8.5–12
420	95–99	250–455	682–737	2.3–2.7
Fe–Mn	60.7	190	228	—
Inconel 625	98.9–99.6	327–376	612–644	40.9–47
Ti–6Al–4 V	—	790	890	8
Copper	85.5	—	116.7	—
Tungsten	97	420	427	—

Source: Adopted from Li et al. (2020).

While assessing the mechanical properties of MBJ-printed parts is crucial, the amount of relevant research in this domain is still limited, particularly in comparison to PBF and DED studies. The microstructures and mechanical properties of MBJ-printable materials, specifically, iron alloys, nickel alloys, titanium and its alloys, copper and its alloys, and refractory metals, are discussed herein. The tensile properties of typical MBJ-printable materials are summarized in Table 6.3.

6.6.1 Iron Alloys

Iron alloy powders, such as 304, 316, 347, 420, 430, and 17-4 PH, are the most widely employed powders in MBJ. Since achieving a high packing density of the powder bed in MBJ is challenging, the high porosity in MBJ-printed parts constitutes a common issue. The porosity of the printed parts is associated with several factors, including the selection of the raw powder and the post-sintering process.

The size of the powder particles defines the sinterability of the green parts and their final pore sizes. For example, fine 316 powder with particle sizes of 22–31 μm was found to densify at low sintering temperatures compared to coarser powders with particle sizes of 20–53 and 45–90 μm (Verlee et al. 2012). The resultant densification of the three powders decreased as the average size of their particles increased, and a concomitant increase in large open pores was observed. In addition, irregularly shaped powder particles contributed to a lower powder bed packing density, resulting in the increased porosity of the parts after sintering.

In addition to the size and shape of the powder particles, the post-sintering temperature, duration, and profile can also influence the porosity of the final parts. For example, a higher relative density of ~98% was achieved in 316 parts when the sintering temperature increased from 1255 to 1400 °C, which also corresponded to

an increase in their tensile strength from 310 to 520 MPa and their elongation from 21% to 62%.

Achieving high porosity in printed parts may be desirable for applications such as tissue engineering, thereby introducing the necessity of proper porosity control. To this end, Ziaee et al. (2017) employed fine 316L powder to print green parts of varied densities and controlled shrinkage levels via MBJ. Raw 316L powder (smaller than 22 μm) was selected to prepare different powder types, namely, agglomerate powders with particle sizes of 25–45 μm cured at different temperatures and 316L/polyamide mixed powders (average particle size of 55 μm) with different volumetric ratios.

The printed green parts were initially processed at 800 °C to remove the polyamide. Subsequently, they were sintered in an argon/hydrogen gas atmosphere at 1360 °C for 60 minutes. The parts printed from raw 316L powder and an agglomerated powder cured at 185 °C obtained similar spread density values ($\sim 56\%$) and final relative density values ($\sim 93\%$) after sintering (Figure 6.8a). However, a low spread density of 42% was attained for parts printed from an agglomerated powder cured at 100 °C, which exhibited a final density of only 77% after sintering (Figure 6.8b). The polyamide served as a fugitive space holder, and its addition was advantageous for preparing porous structures. Notably, the printed 316L parts with 25% and 33% polyamide displayed a density of 66.8% and 63.3%, respectively, after sintering (Figure 6.8b). The polyamide served as a fugitive space holder, and its addition was advantageous for preparing porous structures. Notably, the printed 316L parts with 25% and 33% polyamide displayed a density of 66.8% and 63.3%, respectively, after sintering. High shrinkage of these parts was observed along the build direction, indicating that more pores existed between the powder layers than within them.

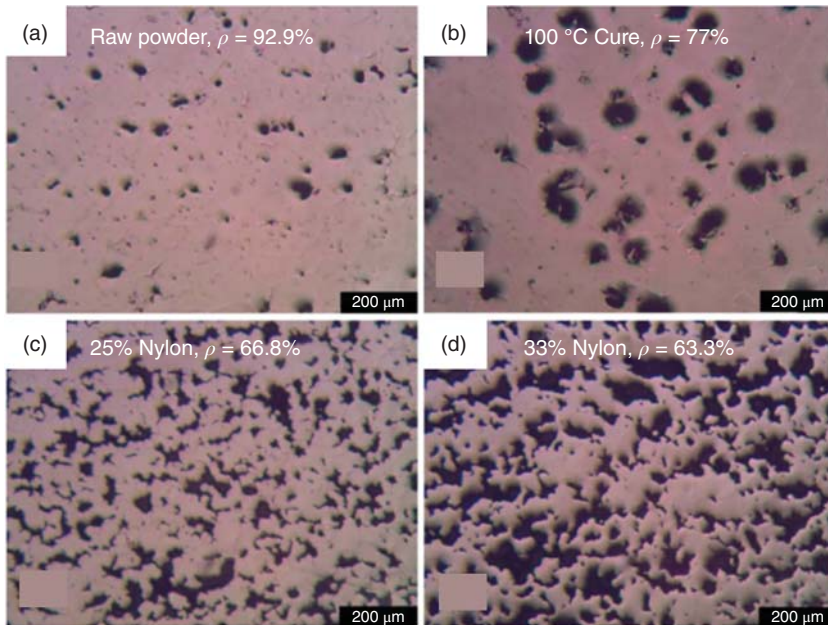


Figure 6.8 Pores of sintered samples printed from (a) 316L, (b) powder agglomerates cured at 100 °C, and (c, d) 316L/polyamide mixed powders with different ratios. Source: Ziaee et al. (2017)/reproduced with permission from Springer Nature.

6.6.2 Nickel Alloys

The weldable nickel-based Inconel 625 and 718 alloys have been widely explored in terms of their compatibility with MBJ and post-sintering properties. For example, Mostafaei et al. (2016) investigated the effects of the sintering temperature on an MBJ-printed Inconel 625 alloy part. At a sintering temperature of 1280 °C, the relative density of the printed part increased from 53% to 99.6%, and its dimensions and volume shrank by ~19% and ~46%, respectively. As the sintering temperature further increased, a liquid phase was formed at the grain boundaries of the printed part, degrading its mechanical properties.

Additionally, grain coarsening occurred in the printed Inconel 625 part when the sintering temperature increased from 1280 °C to 1300 °C, thereby leading to the growth of its grains from 55 to 182 μm . After sintering at 1280 °C, the printed part possessed an ultimate tensile strength of 612 MPa, a yield strength of 327 MPa, and a fracture strain of 40.9%, which are comparable to its cast counterparts. After solution and aging treatment, carbides and Cr_2O_3 precipitates were discovered at the grain boundaries and within the grains, and the printed part possessed a microhardness value of up to ~330 HV, an ultimate tensile strength of ~700 MPa, and an elongation of 30%.

Figure 6.9 shows the schematic of the microstructure evolution of MBJ-fabricated Inconel 625 alloy parts printed from gas- and water-atomized powders (Mostafaei

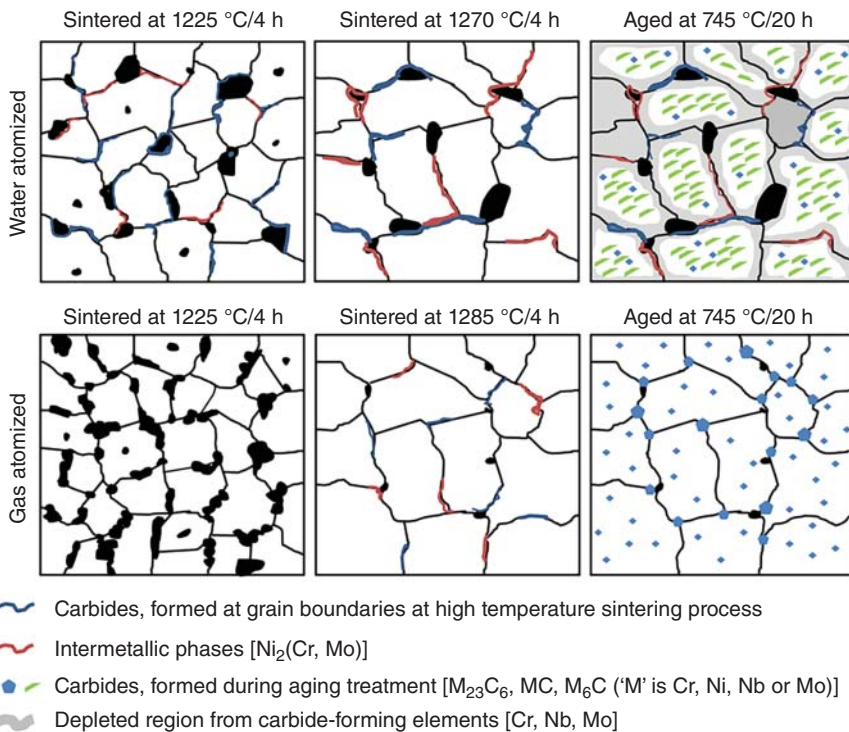


Figure 6.9 Schematic illustration of the microstructure evolution of an MBJ-printed Inconel 625 alloy part using gas- and water-atomized powders. Source: Mostafaei et al. (2017b)/reproduced with permission from Elsevier.

et al. 2017b). At a low sintering temperature of 1225 °C, the parts printed from the gas-atomized powder displayed a large number of fine pores without any visible precipitation of oxides and carbides. In comparison, the parts printed from the water-atomized powder exhibited fewer large pores at their grain boundaries and smaller pores within their grains, which were accompanied by carbide and oxide precipitates.

A further increase in the sintering temperature promoted grain growth in all the parts and eliminated nearly all pores in the parts printed from the gas-atomized powder. After aging, significant precipitation of carbides and oxides occurred at the grain boundaries of the parts printed from the water-atomized powder, thereby depleting the chromium, niobium, and molybdenum contents around the grain boundaries. In contrast, only a small amount of carbide and oxide particles were detected in the parts printed from the gas-atomized powder.

The effects of the layer thickness and sintering temperature on the properties of MBJ-printed Inconel 718 parts were investigated (Turker et al. 2008). An increase in the layer thickness was found to impede the densification of the printed alloy parts. At a sintering temperature below 1260 °C, the parts displayed high porosity. As the sintering temperature increased to 1280 °C, Nb-rich γ'' precipitates were observed at the grain boundaries and within the grains of the printed alloy parts. The increase in the sintering temperature also resulted in precipitate dissolution along the grains and the consequent formation of residual pits. The relative density and linear shrinkage of the printed alloy parts at a sintering temperature of 1280 °C were 98% and 19.5%, respectively.

The powder characteristics of Inconel 718, such as the sizes of the powder particles and their distribution, also play important roles in determining the mechanical properties of MBJ-printed parts (Nandwana et al. 2017). For example, at the same sintering temperature, smaller powder particles underwent greater linear shrinkage than larger powder particles. Therefore, a powder particle size distribution with a high fraction of small powder particles corresponds to a high powder bed density.

Non-weldable nickel-based superalloys with high amount of ordered $\text{Ni}_3(\text{Al}, \text{Ti})-\gamma'$ are desirable for applications in the aerospace and energy domains because of their excellent mechanical performance under high temperatures. However, such non-weldable superalloys are highly susceptible to hot cracking when processed through techniques such as PBF (Chauvet et al. 2018). In the MBJ process, the consolidation of powder particles does not require material melting, thereby allowing residual stress and thermal gradients within the printed parts to be significantly reduced. Therefore, MBJ is superior to PBF in circumventing the issue of hot cracking in non-weldable nickel alloy parts.

For example, the Ni-based RENÉ 108 alloy, also named as CM247LC or Mar M 247, generally possesses a γ' volume fraction of over 60%, which promotes crack formation during PBF. Recently, a green RENÉ 108 part with a relative density of 60–62% was fabricated and further densified, resulting in a relative density of 96% after post-sintering and almost 100% after further HIP treatment (Martin et al. 2021). Consequently, the final part was free of cracks and exhibited thermo-mechanical properties on par with conventional parts manufactured via

directional solidification. However, the formation of carbon residue remains an issue for MBJ. A critical debinding operation is necessary to remove such residue, particularly for superalloys containing high amounts of reactive alloying elements such as titanium and tantalum.

6.6.3 Titanium and Its Alloys

MBJ-printed parts composed of titanium and its alloys are mainly investigated for bone implant applications due to their porous structures. A pure titanium implant printed via MBJ was found to possess a stiffness of 2–30 GPa and a compressive strength of 130–180 MPa, which are similar to those of human bones (Xiong et al. 2012). In the study, titanium powder (200 mesh, smaller than $74\text{ }\mu\text{m}$) and an aqueous polyvinyl alcohol powder binder (20 mesh, smaller than $125\text{ }\mu\text{m}$) were mixed and employed as the raw material.

In another study, a mixed powder composed of 97 wt% titanium powder with a particle size distribution of $75\text{--}90\text{ }\mu\text{m}$ and 3 wt% polyvinyl alcohol powder with particle sizes below $63\text{ }\mu\text{m}$ was prepared (Sheydaeian et al. 2017a). The porosity and shrinkage of the printed parts increased as the layer thickness increased from 80 to $150\text{ }\mu\text{m}$, while the yield stress only underwent a minor reduction from 175 to 158 MPa.

A combination of MBJ and material extrusion was explored to fabricate porous titanium parts (Sheydaeian et al. 2017b). Sacrificial polymer droplets were jetted periodically onto certain powder layers to create cellular titanium structures with closed cavities. Such structures exhibited an elastic modulus of 2.48–3.55 GPa and a yield strength of 107.65–145.75 MPa, which are comparable to those of cancellous bones. In a similar study, a titanium boride slurry was employed in place of the polymer droplets to manufacture TiB_2/Ti composite parts (Sheydaeian and Toyserkani 2018). The stiffness of the printed composite parts underwent an increase of up to 15.2% when a small fraction (4%) of TiB_2 powder was added to the binder.

The relative density of the MBJ-printed Ti–6Al–4V part varied from 50% to 95% (Stevens et al. 2018), for which the binder and powder effects could be considered as the main factors leading to such variations (Figure 6.10). The binder droplets disrupted and distorted the powder layer, adversely affecting the quality of the printed parts. Meanwhile, the presence of satellites in the gas-atomized powder reduced

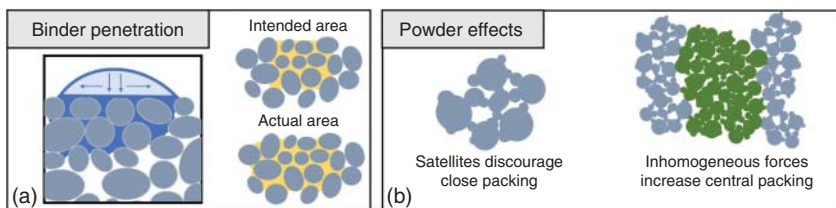


Figure 6.10 Schematic illustration showing (a) the interaction between the binder and the powder bed and (b) powder effects on the part density. Source: Reproduced from Stevens et al. (2018)/with permission from Elsevier.

the packing efficiency. Differences between the absorbed loads on the core areas and the edges could also affect part densification.

6.6.4 Copper and Its Alloys

Copper and its alloys are particularly suitable for manufacturing products via MBJ. Due to their high thermal conductivity and laser reflectivity, it is relatively difficult to process copper and its alloys through laser-based PBF and DED.

The influences of the powder particle size and the ratio of bimodal copper powder mixtures on the density of the final parts and the extent of their shrinkage have been investigated (Bai et al. 2017). In theory, utilizing bimodal or trimodal powder mixtures can increase the density of green parts and reduce their shrinkage during the sintering process, which is achieved by improving the powder bed density and filling the interstitial gaps between coarse particles with fine particles.

In another study, fine copper powder with an average particle size of 15 μm was selected for printing parts via MBJ, which were sintered at 1080 $^{\circ}\text{C}$ (Bai and Williams 2015). The printed parts displayed a mechanical strength of ~ 117 MPa, which was much lower than that of their injection-molded counterparts (200 MPa).

HIP can be conducted to further densify MBJ-printed copper parts (Kumar et al. 2018), and a maximum increase of 8% in their density can be achieved. For example, different copper parts printed using a 17- μm powder and a bimodal powder (prepared from 5- μm to 30- μm powders) underwent an increase in density from $\sim 84\%$ to $\sim 86\%$ and from $\sim 91\%$ to $\sim 98\%$, respectively, after HIP. Compared to a fully dense part composed of sintered copper powder with a tensile strength of 220 MPa, the bimodal HIP sample displayed a tensile strength of ~ 177 MPa and an elongation of $\sim 31\%$.

In another study, the impact of process-induced porosity on the material properties of copper parts printed through MBJ was investigated (Kumar et al. 2019). The copper parts obtained a relative density of 97.3% after HIP was performed at a temperature of 1075 $^{\circ}\text{C}$, a pressure of ~ 207 MPa, and a holding time of two hours. The high relative density of the parts corresponded to a high tensile strength of 176 MPa and a thermal conductivity of ~ 328 W/mK, which are $\sim 80\%$ and $\sim 85\%$ of those of a wrought copper alloy, respectively.

MBJ-printed copper parts processed separately with a polymeric binder and a MOD ink were compared (Bai and Williams 2018). The MOD ink facilitates the formation of an organometallic compound by introducing ligands to metal salts. Therefore, it could improve the solubility of metal–organic compounds in saturated solvents, thereby increasing the metal content in the binder. Note that the MOD ink is a particle-free ink, and thus nozzle clogging and sedimentation did not hinder the printing process.

Figure 6.11a illustrates the printing, curing, and sintering stages. During the curing stage, nanoparticle precipitates are formed from the MOD ink, and interparticle necks are formed at a sintering temperature of 150–300 $^{\circ}\text{C}$ in the case of copper nanoparticles, thereby enhancing the strength of the green parts. Figure 6.11b shows the cross-sectional images of a printed part processed with MOD ink, revealing large

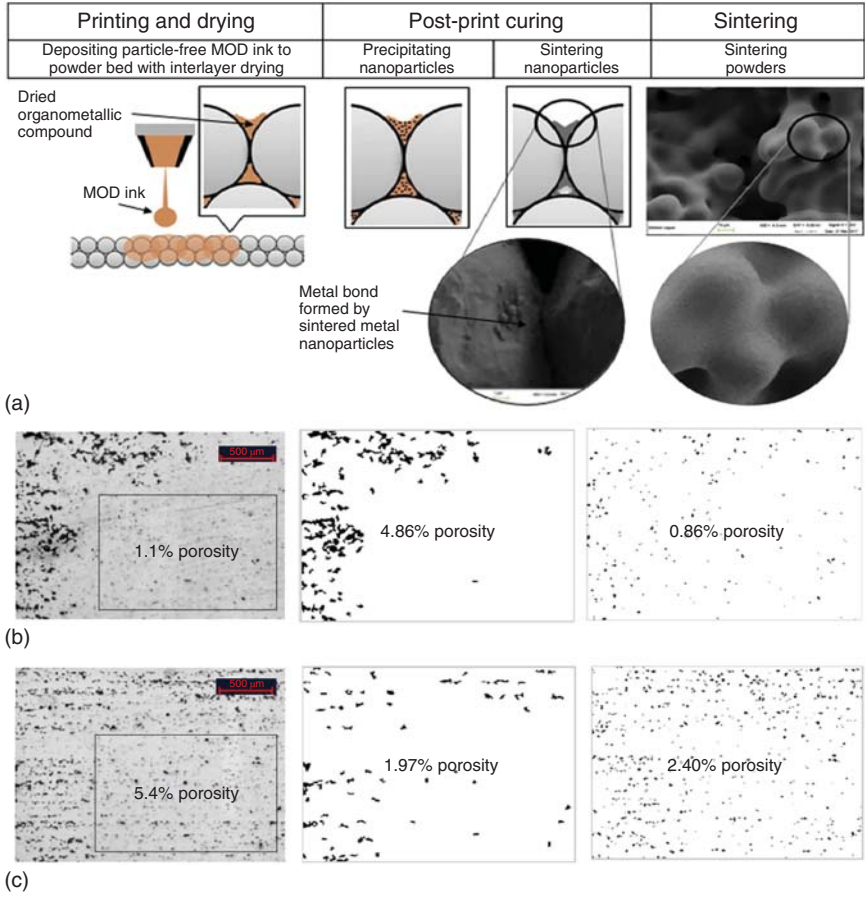


Figure 6.11 (a) Schematic of the printing and curing stages with a MOD ink as the binder and SEM images of the sintered nanoparticles and powder particles. Cross-sectional images displaying the porosity of printed parts processed with (b) a MOD ink and (c) a commercial binder. Source: Bai and Williams (2018)/reproduced with permission from Elsevier.

pores near its surface. Meanwhile, parts printed using a commercial binder possess randomly distributed pores (Figure 6.11c).

6.6.5 Refractory Metals

Refractory pure metals and alloys are often categorized as difficult-to-print materials for laser-based AM. For example, tungsten heavy alloys (WHAs) include refractory tungsten and other alloying elements such as nickel, iron, and copper, which exhibit limited solubility and a wide range of melting temperatures (Iveković et al. 2019). As a result, significant issues regarding elemental vaporization and creation of cracks may arise during the PBF processing of such alloys. The MBJ printing process does not involve metal powder fusion to achieve densification, thereby providing an alternative approach that circumvents the aforementioned issues.

For instance, a green part was printed from a W–Ni–Cu–Fe heavy alloy via MBJ and subsequently dewaxed in a reducing atmosphere at a maximum temperature of 870 °C (Stawovy et al. 2019). After further sintering at 1385 °C, crack-free W–Ni–Cu–Fe parts with a relative density of 99.7% and an average tensile strength of 770 MPa were obtained. The density and mechanical performance of these parts matched the specifications of ASTM B777 for WHAs.

Another refractory material processable by MBJ is tungsten carbide–cobalt (WC–Co). This ceramic–metal composite possesses excellent hardness, fracture toughness, and flexural strength, rendering it particularly effective as a material for machining, cutting, and drilling. A recent study indicates that a combination of binder jetting and post-heating treatment can produce defect-free WC–Co parts with a uniform microstructure and superior mechanical properties (Mostafaei et al. 2021a). Despite the low relative density (21–23%) of the printed green WC–Co parts, a relative density of nearly 100% was achieved through sintering at 1435 °C, followed by HIP under a pressure of 6.1 MPa.

6.6.6 Others

Magnesium alloys, as some of the lightest biodegradable engineering metallic materials, display great potential for fabricating medical implants and lightweight automobile parts. Most research on AM-printed magnesium (Hu et al. 2015) and its alloys, such as WE43 (Li et al. 2018), Mg–Al (Niu et al. 2018), and Mg–Zn (Wei et al. 2019), was conducted using laser-based AM. However, due to their intrinsic properties, such as a strong affinity for oxygen and high vapor pressure, magnesium parts are subjected to oxidization and element evaporation during laser-based AM processes, which may change their chemical composition and cause the formation of gas pores. As a beamless printing technique capable of fabricating parts at near room temperature, MBJ is a suitable candidate for printing parts from magnesium and its alloys. For example, Salehi et al. have printed Mg–Zn–Zr parts via MBJ using capillarity-driven bridging as a novel and efficient tool for assembling powder particles into 3D structures while minimizing the metallurgical complexity (Salehi et al. 2019b). In another work by Su et al. (2021) MBJ was employed to print Mg–Al–Zn (AZ91D) parts, which were subsequently processed through a two-step sintering strategy that drastically enhanced their relative density, mechanical property, and corrosion resistance compared to conventional one-step sintering.

A limited amount of research has been conducted on the MBJ processing of cobalt-based alloys. In a study, an MBJ-printed Co–Cr–Mo alloy part achieved a relative density of ~99.7% and a microhardness of ~322 HV after undergoing HIP (Stoyanov et al. 2016). The effects of binder saturation and post-heat treatment on the relative density and microstructure of Co–Cr–Mo alloy parts were also explored (Sears et al. 2019). The printed parts with a binder saturation level of 95–100% were partially melted at a sintering temperature of 1325 °C. After sintering, the linear shrinkage values along the *x*, *y*, and *z* directions were calculated to be ~19.4%, 18.8%,

and 22.3%, respectively. The yield strength, ultimate tensile strength, and elongation of the sintered Co–Cr–Mo parts were measured to be 462 MPa, 730 MPa, and 12%, respectively.

A sintered Co–Cr–W alloy component fabricated through MBJ using powder with an average particle size of $\sim 95\text{ }\mu\text{m}$ exhibited an ultimate tensile strength of ~ 850 and 885 MPa before and after aging, respectively (Mostafaei et al. 2019). Such a difference can be attributed to variations in the microstructure after the aging treatment, during which the γ phase (face-centered cubic, FCC) was transformed into the ϵ phase (hexagonal close packing, HCP).

Nickel–manganese-based ferromagnetic shape memory alloys display magnetocaloric and magnetic shape memory effects (Dey et al. 2016). A pre-alloyed angular Ni_{49.6}Mn_{30.8}Ga_{19.6} ball-milled powder with particle sizes below $63\text{ }\mu\text{m}$ was fabricated by MBJ and sintered at 1020°C (Mostafaei et al. 2017a). During sintering, interparticle necks were formed, and no manganese was evaporated. Notably, the sintering process could be optimized without incurring any element loss.

A soft magnetic Fe–6Si powder was selected to fabricate geometrically complex, crack-free magnetic parts via MBJ, which obtained a relative density of $\sim 99\%$ after solid-state sintering (Cramer et al. 2019). These parts exhibited reduced core loss at various frequencies, high resistivity, and good magnetic permeability. Notably, their grain size was measured to be $56.3\text{ }\mu\text{m}$. The printed parts attained an ultimate tensile strength of 434 MPa , an electrical resistivity of $98\text{ }\mu\Omega\text{ cm}$, a saturation magnetization of 1.83 T , a low coercivity of 0.4 Oe , and a maximum relative permeability of 10.5 . The results indicate that MBJ-printed soft magnetic Fe–6Si parts could be an alternative to silicon steel parts fabricated by chemical vapor deposition.

A neodymium–iron–boron magnetic powder with an average particle size of $\sim 70\text{ }\mu\text{m}$ was synthesized and explored for MBJ purposes (Paranthaman et al. 2016; Li et al. 2017), and Nd₂Fe₁₄B phases were identified in both the raw powder and the printed parts. The volume fraction of the printed parts was measured to be ~ 0.45 with a remanence of $\sim 0.3\text{ T}$.

High-entropy alloys (HEAs) are potential candidates for printing parts via the MBJ process (Han et al. 2020). However, the amount of research conducted on this topic is still limited. In a study, an AlCoCrFeNi HEA part with a porosity of $\sim 1\%$ was printed through MBJ before sintering (Karlsson et al. 2019), and it was determined to be only stable as a single phase within a narrow temperature range below its melting point. Notably, the as-sintered HEA part displayed a dominant B2 phase (body-centered cubic, BCC), with an additional FCC phase located at its grain boundaries and σ -phase precipitates within its grains. An increase in the annealing temperature further suppressed the expansion of the FCC phase within the HEA part, thereby increasing its yield strength from 1203 to 1461 MPa and its fracture strength from 1996 to 2272 MPa . Additionally, the HEA part obtained an excellent oxidation resistance, with the oxide layers exhibiting a thickness below $5\text{ }\mu\text{m}$ after 20 hours of annealing.

6.7 Summary

MBJ possesses certain advantages over other metal AM methods by eliminating the residual thermal stress in the printed parts and providing a reasonable balance between the productivity and resolution. Additionally, an inert atmosphere is not required for the shaping process. Therefore, compared to PBF processes, extending the build chamber of an MBJ system to print large parts is relatively simple. Furthermore, the applicability of MBJ extends to materials that are difficult to print via PBF, which include non-weldable alloys, pure copper, and refractory metals. However, MBJ merely serves as a complementary technique to PBF and DED instead of their successor, allowing AM to infiltrate traditional metalworking sectors dominated by sintering, such as metal injection molding and powder metallurgy. The existing sintering facilities and parameters can be reutilized for MBJ purposes.

Despite the aforementioned advantages of MBJ, steps must be taken to address its drawbacks, especially with regard to improving the density of the final parts and manipulating their shrinkage during the sintering stage. So far, the amount of research dedicated to the MBJ process is still insufficient, and such inadequacy is manifested in the lack of understanding of its raw materials (powders and binders), building parameters, post-processing (curing and sintering), and numerical modeling.

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7

Applications

The development of metal powder-based additive manufacturing (AM) techniques has progressed rapidly in recent years, and these techniques have been employed in a broad range of industrial applications, indicating their tremendous potential to revolutionize the global manufacturing framework while offering reduced production costs, low energy consumption, and high degrees of customization. This chapter discusses the latest advances in metal powder-based AM products in the aerospace, biomedical, automotive, molding and tooling, energy, jewelry, marine, and oil and gas industries, providing insights of both academic and industrial relevance.

7.1 Aerospace

Research and development sectors within the aerospace industry primarily focus on improving the efficiency of aircraft and reducing air and noise pollution (Behlau 2009). Typical characteristics of aircraft components include complex geometries and large envelope-to-volume ratios, being difficult to machine with high buy-to-fly ratios, small production runs, quick turnaround time, and high performance. Therefore, AM is highly suitable for the fabrication of aircraft components. For example, leading aerospace corporations such as Boeing and Airbus have implemented AM to reduce the production time, construct lighter-weight parts, and lower the operational costs.

Current operations within the aerospace industry include concept modeling, concept prototyping, and low-volume fabrication of complex parts, such as airfoils with embedded cooling channels, engine turbines with intricate internal structures for cooling purposes, and combustion chambers and turbine blades exhibiting thin-walled structures and large envelope-to-volume ratios. Because of these features, the tool path planning algorithm of conventional computer numerical control (CNC) machining is typically complicated and computationally inefficient. Parts manufactured by AM can be quickly shipped and installed in damaged aircraft to resume operation. According to Airbus, the turnaround time for testing or replacing parts can be as short as two weeks.

Aviation components are typically made of lightweight materials with a high strength-to-weight ratio to improve the fuel efficiency and reduce emissions. Some components are subjected to extreme working conditions, such as ultrahigh/low temperatures or hazardous chemical environments. In particular, engine components are constantly under very high temperatures, and their constituent materials are required to contain flame retardants. Laser-based directed energy deposition (L-DED), powder bed fusion (PBF), and metal binder jetting (MBJ) are popular metal powder-based AM techniques employed in the aerospace industry. These techniques commonly involve materials such as titanium alloys, nickel-based superalloys, aluminum alloys, and special steels.

High-performance aerospace components, such as compressors, blisks, turbines, blades, and airfoils, are usually expensive to manufacture because of the high market value of the materials required (e.g. Ti-6Al-4V and Inconel 718) and the complex manufacturing process involved. Aerospace components may be subjected to corrosion, impact, variable thermal cycles and stresses, and other conditions that could create cracks within them. Fatigue and stress cracks are common initiators of failure in high-performance components that result in them being scrapped. Because of the high cost of materials and labor involved in fabricating such high-value components, it is necessary to repair them whenever possible instead of replacing them.

L-DED is highly suitable for repairing high-value aerospace components. Its basic principle involves utilizing a laser beam to create a metallurgical bond between the damaged surface area of a component and the repair materials (e.g. metal powders). The powder is locally deposited onto the defect area according to its geometry. Compared to conventional repair techniques, L-DED requires a low heat input, leading to the formation of a small heat-affected zone in the surrounding substrate materials, which in turn causes minimal distortion that is ideal for manufacturing thin-walled structures, such as aircraft wing spars and bulkheads.

The company Optomec provides solutions for repairing damaged aircraft engine components through L-DED, which can precisely supply powder to worn-out components and restore their geometry. Integrally bladed rotors, also known as blisks, are high-value components that may each cost US\$10 000–100 000 to fabricate. Typically, a single worn-out airfoil results in an entire blisk being scrapped. However, L-DED can be employed to repair such wear. For example, a T700 blisk made of AM355 steel, whose airfoil leading edges had undergone erosion during service, was successfully repaired through L-DED. Figure 7.1a–c illustrates the repair process of the leading edge of a Ti-6Al-4V airfoil, the blisk after deposition, and the blisk after surface finishing. In this case, Optomec selected a cobalt-based wear-resistant material to repair the leading edge.

Fraunhofer ILT has been successfully certified by Rolls-Royce Deutschland for fifteen different repair applications, which include repairing the BR715 high-pressure turbine and BR715 high-pressure compressor front drum. Geometric features on the surface of a BR715 high-pressure turbine case, such as bosses, brackets, and flanges, are repaired locally with just one layer of deposit. Because of the minimized heat input of the L-DED process, distortion can be almost completely avoided. In addition, L-DED can reduce contamination/oxidation by implementing

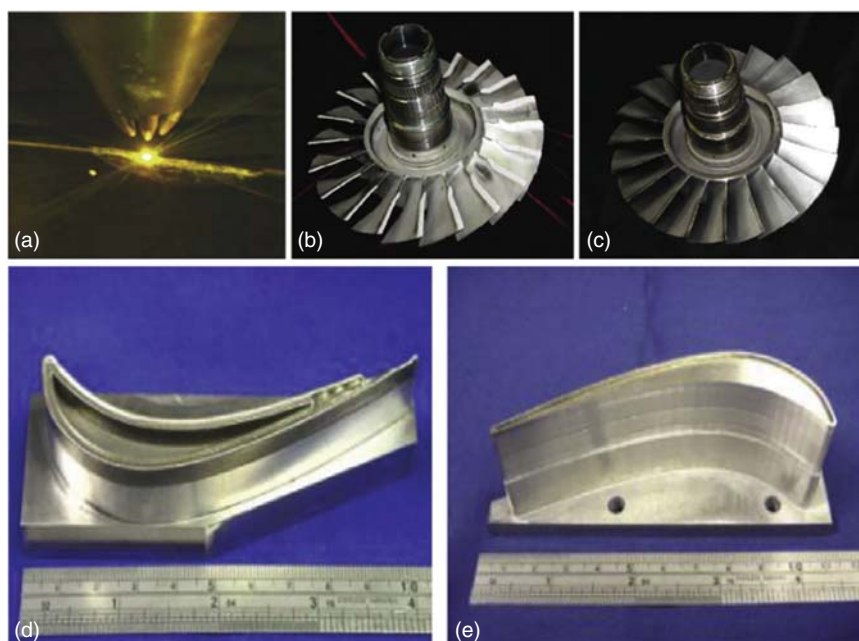


Figure 7.1 Repair of a T700 blisk using the laser engineering net-shaping process. (a) In-process repair of the leading edge of a Ti-6Al-4V airfoil, (b) the blisk after deposition, and (c) the blisk after finishing. Source: Reproduced with permission from Optomec, Inc. (d) Damaged tip and (e) repair of a cast IN738 blade. Source: Xue and Islam (2002)/reproduced with permission from Metal Powder Industries Federation.

proper local gas shielding through a newly developed powder nozzle. Universities and research institutes have also been investigating the usage of L-DED for repair applications in the aerospace industry. Figure 7.1d,e present the tip and seal of a damaged IN738 blade that was repaired through L-DED (Xue and Islam 2002).

RPM Innovations conducted a low-wattage (below 500 W) repair process of a Ti-6Al-4V bearing housing unit within a gas turbine engine using L-DED. The region surrounding the bearing seat was worn beyond standard tolerance limits, and the entire component was initially considered scrap. L-DED was first employed to restore the worn area, followed by machining to meet the tolerance requirements. The housing unit was successfully repaired with no measurable distortion, and its functionality was validated by a test engine. The repair cost was about 50% lower than the price of a new housing unit, and the repair process took only a few days. In comparison, several weeks are required for a new unit to be delivered.

L-DED has also been employed to repair an Inconel 718 gas turbine compressor seal unit, which is a critical high-value component that prevents gas leakage in gas turbine engines (Mudge and Wald 2007). The labyrinth seal in the system underwent excessive wear, which adversely affected the performance of the gas turbine. After being repaired and machined to reach standard tolerance levels, the compressor seal unit was approved for consumer use. The cost of repairing the compressor seal was determined to be 45% of a new unit, indicating the cost-saving capability of L-DED.

repair processes. Additionally, a turbine airfoil was repaired and remanufactured by L-DED through a novel semi-automated geometric reconstruction algorithm, which also demonstrates the effectiveness of L-DED in repairing defective voids in turbine airfoils (Wilson et al. 2014).

An overhaul and repair method was proposed to restore the complex geometry of expensive aerospace components, which include critical aero-engine components such as thin-curved compressor blades (Yilmaz et al. 2010). This methodology involves a three-dimensional (3D) noncontact digitization and free-form surface reconstruction process using L-DED and milling operations in an automatic hybrid process. It was discovered that the total repair time of the proposed repair methodology is 30% lower than that of conventional repair methods, thereby rendering it a relatively efficient, reliable, and cost-effective approach.

In addition to repair applications, the direct fabrication of aviation components is another essential role of metal powder-based AM in the aerospace industry. The Welding Institute (TWI), an independent research organization, adopted the L-DED process for manufacturing overhanging structures without support mechanisms. A helicopter engine combustion chamber, which is a thin-walled structure, was successfully printed through L-DED (Figure 7.2a). The mechanical testing indicated that the wall density throughout the finished product exceeded 99.5%. Meanwhile, the build time of the part printed by L-DED was about 7.5 hours, while the conventional substrate machining of the same part requires months to complete.

Figure 7.2b presents a turbine housing unit composed of stainless steel fabricated through a LASERTEC 65 3D hybrid manufacturing system developed by DMG Mori (Germany). The dimensions of the turbine housing unit are $180 \times 150 \text{ mm}^2$, and the build-up time for deposition and milling were 230 and 76 minutes, respectively. This hybrid manufacturing process produces quality parts by combining the precision of CNC machining and the free-form fabrication capability of the AM process. Figure 7.2c displays a 1/6 scale mixing nozzle of the gas turbine exhaust system of a Bell helicopter, which was manufactured by Optomec through L-DED. Meanwhile, a Ti-6Al-4V airfoil with embedded cooling channels was fabricated by Xue and Islam (2006), as shown in Figure 7.2d.

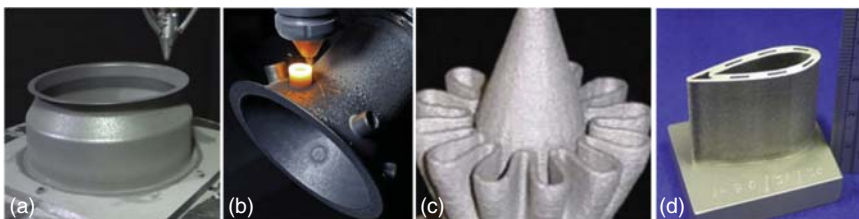


Figure 7.2 (a) IN718 helicopter engine combustion chamber. Source: Reproduced with permission from TWI Ltd. (b) Turbine housing unit. Source: Reproduced with permission from DMG Mori. (c) 1/6 scale mixing nozzle for a gas turbine exhaust system. Source: Reproduced with permission from Optomec, Inc. (d) Ti-6Al-4V airfoil with embedded cooling channels. Source: Xue and Islam (2006)/reproduced with permission from Metal Powder Industries Federation.

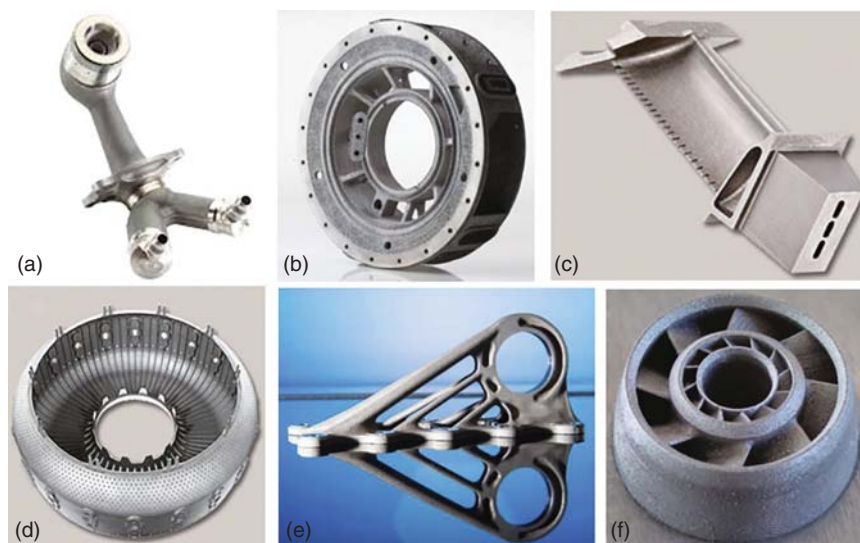


Figure 7.3 (a) GE LEAP engine fuel nozzle fabricated through LPBF. (b) Compressor supporting casing for a gas turbine engine fabricated by EBM. (c) LPBF-printed turbine blade with internal cooling channels, (d) LPBF-printed engine housing unit, and (e) the first LPBF-printed titanium bracket connector for the Airbus A350 XWB. Source: Reproduced with permission from General Electric. (f) Hollow static turbine blade cast with its mold and cores fabricated by MBJ. Source: Reproduced with permission from PROMETAL S.A.R.L.

A wide range of PBF AM materials, including stainless and tool steels, titanium and its alloys, nickel-based alloys, and certain aluminum alloys, are employed in the aerospace industry. For example, General Electric (GE) Aviation manufactures next-generation jet engine components through the laser powder bed fusion (LPBF) process. The newly printed fuel nozzle of a “Leading Edge Aviation Propulsion” (LEAP) engine produced by GE is shown in Figure 7.3a. Compared to conventional fuel nozzle designs, the LPBF-designated nozzle design integrates 18 components with complex passageways, thereby reducing the number of brazes and welds from 25 to 5. As a result, the weight of the LPBF-printed nozzles is 25% less than that of their predecessors. Each LEAP engine includes 19 nozzles, and GE Aviation has set the goal of fabricating 32 000 nozzles per year. This number has been increased to 100 000 by 2020, during which GE has reached full production capability. A total of US\$3.5 billion has been invested in new industrial plants to produce LEAP engine nozzles, whose functionality has already been assessed. On a different note, 35% of the components of an advanced turboprop demonstration engine that powers the state-of-the-art Cessna Denali single-engine aircraft are fabricated by AM, which corresponds to a weight reduction of 5% and a specific fuel consumption improvement of 1% (General Electric 2016).

Using titanium alloys, Arcam applies its electron beam melting (EBM) technology to manufacture various functional components, including commercial and military aircraft components, aerospace devices, missiles, and various subsystems (e.g. engines and accessories). An EBM-printed Ti-6Al-4V compressor supporting

casing for a gas turbine engine is shown in Figure 7.3b. Concept Laser, a subsidiary company of GE, utilizes LPBF to print Inconel 718 turbine blades, which are typical thin-wall components containing complex channels (Figure 7.3c), and an engine housing unit (Figure 7.3d). A bracket connector prototype (designated for AM) developed by Concept Laser for the Airbus A350 XWB is displayed in Figure 7.3e. Compared to conventional designs that are realized through casting or milling, this prototype boasts 30% lighter weight due to its porous structure, thereby reducing the fuel consumption and increasing the load capacity of the aircraft. In addition, the toolless fabrication of the connector through LPBF is relatively inexpensive and expeditious, requiring only approximately a month to complete. In contrast, conventional designs correspond to a development time of up to six months.

A large build volume and high build rate are characteristics of MBJ, which render the low-volume production of metal-based casting prototypes (typically composed of aluminum and copper alloys, gray and ductile iron, and magnesium and its alloys) a reality. Based on a report by ExOne, MBJ can be employed to fabricate complex gear cases and covers, fuel tanks, transmission housing units, certain components containing draft-free walls, lightweight engine parts, and structural hinges. For example, the mold and cores of a hollow static turbine blade in Airbus A320 were manufactured through MBJ (Figure 7.3f).

The fabrication of spacecraft and satellites has always entailed the most advanced technologies. With the knowledge that AM can satisfy the stringent requirements of the aerospace industry while remaining cost-efficient, an increasing number of companies are venturing into this domain. Figure 7.4a shows a full-scale copper rocket engine component printed through LPBF by the National Aeronautics

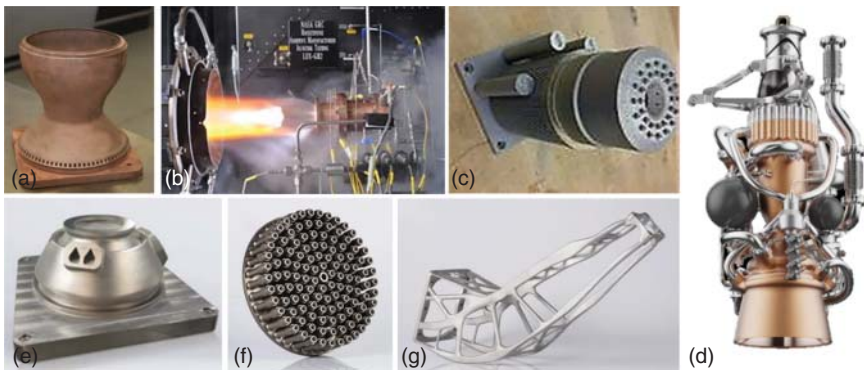


Figure 7.4 Typical LPBF-printed components for the aerospace sector. (a) Copper rocket nozzle, (b) testing a printed rocket nozzle, and (c) rocket injector printed using an Inconel steel powder. Source: Reproduced with permission from NASA. (d) Combustion chamber assembled with printed copper components and conventionally manufactured components. Source: Reproduced with permission from Launcher. (e) Injector head of the all-in-one design of a rocket engine with 122 injection elements using EOS Nickel Alloy IN718 and (f) Ariane 6 baseplate for function integration. Source: Reproduced with permission from ArianeGroup. (g) Al-Si10-Mg satellite bracket. Source: Reproduced with permission from RUAG Group.

and Space Administration (NASA) in 2015, which was designed to operate under extreme temperature and pressure. In 2005, Aerojet Rocketdyne manufactured and conducted the hot-fire test of a rocket engine, whose thrust chamber was composed of a copper alloy and printed through LPBF. The AR1 single-element hot-fire tests were conducted at an excess of 2000 psi, which corresponds to the highest pressure for rocket engine applications. In producing the main injector alone, LPBF offers the potential for a nine-month reduction in part lead time and a 70% reduction in cost.

Figure 7.4b presents a liquid oxygen/gaseous hydrogen rocket injector assembly built through AM and hot-fire tested at the NASA Glenn Research Center. Significant costs may be reduced by decreasing the number of certified parts and processes, such as joining, which are required to manufacture a component. In addition, weight reduction of the product can result in significantly lower fuel consumption when escaping the gravitational force of the Earth. NASA engineers at the Marshall Space Flight Center in Huntsville adopted LPBF to fabricate a rocket injector using an Inconel steel powder (Figure 7.4c). While traditional subscale rocket injectors are composed of four parts and five welds, each of which requires six months to produce and costs over US\$10 000, the construction of the LPBF-printed injector was completed in about 40 hours for less than US\$5000.

In collaboration with EOS and Additive Manufacturing Customized Machines (AMCM), a US start-up company, Launcher, is searching for more efficient methods of launching small-to-medium-sized payloads into space. Using AMCM's M4K machines, Launcher additively manufactured a rocket engine combustion chamber with an integrated nozzle-and-neck system from a copper alloy. At a height of 86 cm and an outlet nozzle diameter of 41 cm, the product was the largest single-piece combustion chamber for liquid rocket engines in the world (Figure 7.4d).

ArianeGroup is responsible for developing and producing Ariane 6, a new European launch vehicle for placing heavy payloads, such as communication satellites, into geostationary orbit. The internals of a propulsion module are subjected to tremendous forces and extreme conditions, and they are required to attain maximum levels of reliability and precision. The injection head is a core element of a propulsion module, and its role is to feed the fuel mixture to the combustion chamber. The traditional design of the injector head consists of 248 components, which are produced and assembled in different manufacturing steps. Additionally, the conventional production of injector heads requires over 8000 cross holes to be drilled in copper sleeves that are subsequently precisely screwed into 122 injector elements for mixing hydrogen gas. EOS printed a single injector head unit through LPBF, which possessed integrated base and front plates, 122 injection nozzles, and a distribution dome with corresponding feed pipes for hydrogen and oxygen fuels (Figure 7.4e,f). Consequently, a quantum leap in its lead time was achieved, with each iteration reduced from approximately half a year to a few days (a reduction of 131 days) at half the cost.

The Swiss RUAG group aims to develop an extremely lightweight and robust antenna bracket for Sentinel satellites. In collaboration with EOS, such a prototype was printed from Al-Si10-Mg powder through LPBF after topology optimization

(Figure 7.4g). The as-printed product exceeded the minimum rigidity requirement for satellite antenna brackets by over 30%, which renders it capable of transmitting strong radio signals to the Earth even after a turbulent flight, assuming that an ideal antenna position has been attained previously. Such high rigidity can be attributed to the highly uniform stress distribution within the satellite antenna bracket, which was achieved through structural optimization simulations. The use of LPBF significantly reduced the weight of the component from 1600 g to 940 g, corresponding to a decrease of over 40%. The component was certified and approved for use in outer space.

7.2 Biomedical

The metal powder-based AM has been applied in the manufacturing of orthopedic and dental implants, which bridges the gap between biology and engineering through the creation of complex biocompatible and bioactive constructs that take advantage of unique material properties (such as osteoconductivity and osteoinductivity) to promote tissue regeneration and implant acceptance. The application of AM in fabricating biomedical implants benefits from its capability to manufacture highly customizable prosthetic components with complex geometries for effective bone integration. Compared to conventional processes, the overall production of a component through powder-based AM is automated to minimize human error and surgical intervention time. A computed tomography (CT) scan is first performed on the affected zone to reconstruct the replacement tissue and convert it into a model to be printed. A polymer model of the region surrounding an implant is normally fabricated with stereolithography, which allows for necessary adjustments to be made to the implant before it is installed, thereby averting the risk of additional surgical interventions. Such changes also benefit the patients during the postoperative period, as they may recover in a shorter duration.

The orthopedic field is one of the biomedical branches that has received the most attention. A few concerns exist regarding common metallic implants that replace load-bearing joints in the knees and hips. In particular, the release of metallic ions from an implant comprising traditional biomedical materials, such as stainless steel, cobalt-chrome, and titanium alloys, can potentially result in hypertension and various undesirable tissue reactions in the patient. Additionally, it is impossible to avoid the wear-induced damage of a metallic implant during its usage. Moreover, installing dense and highly stiff metallic implants exhibiting isotropic mechanical properties can reduce the amount of load distributed to the host bone. Such changes in load distribution lead to stress shielding, which may result in deterioration of the host bone or premature loosening of the implant. Therefore, optimizing the implant design can mitigate the aforementioned hazards to a patient's health.

Among metal powder-based AM processes, LPBF and EBM have been recognized as the most capable in exerting precise control over internal porous structures and achieving complex geometries with tailored properties, which is a major

improvement for orthopedic implants (Han et al. 2020). Furthermore, such porous structures allow for the difference in stiffness between an implant and the host bone to be reduced, which subsequently alleviates stress shielding (Han et al. 2017b, 2018b; Yang et al. 2020). In addition to 316L and cobalt–chrome alloys, titanium and its alloys, such as pure Ti, Ti–6Al–4V, Ti–Nb (Zhao et al. 2020), and Ti–Ta (Zhao et al. 2019, 2021), have been established as the most in-demand metallic biomaterials for printing porous orthopedic structures. The types of unit cells for constructing such porous structures include diamond, hatched, honeycomb-like, cellular, cubic, reticulated mesh, stochastic foam, triangle, hexagonal, rectangular, dodecahedron, rhombic, and triply periodic minimal surface-based structures (Schwarz diamond, Schoen Gyroid, etc.).

The earliest application of LPBF in the orthopedic field occurred in 2005 when an MCP Realizer machine was employed to fabricate a replacement mandible, lumbar vertebra, and tubular femoral bone using 316L stainless steel (Figure 7.5a) (Wehmöller et al. 2005). Figure 7.5b–d present an LPBF-printed Ti–6Al–4V human mandible implant (Bertol et al. 2010), a Co–Cr–Mo talar component for an endoprosthesis ankle device (Liverani et al. 2016), and a customized Ti–6Al–4V ELI frontoparietal-temporal bone implant that precisely restores a patient's cranial defects (Jardini et al. 2014). The endoprosthesis ankle device had undergone a kinematic test on a cadaver leg. The results reveal that the customized articular surfaces of the implant allow it to successfully reproduce natural joint motion, which demonstrates the suitability of LPBF for patient personalization in the scenario of a complete ankle replacement. The fabrication of oral screw-retained implants, hip endoprosthetics, acetabular cups, and other biomedical devices has also validated the applicability of LPBF in the biomedical industry (Vandenbroucke and Kruth 2007; Bertol et al. 2010; Liu et al. 2015).

Figure 7.5e–g show an EBM-printed Co–29Cr–6Mo alloy femoral knee implant made with lattice structures (Murr et al. 2012), acetabular cups printed by Arcam, and a skull plate (Mazzoli et al. 2009), respectively. Using the Arcam EBM technique, Adler Ortho Group launched the CE-certified Fixa Ti-Por acetabular cup in the European market in 2007. Figure 7.5h displays hip stems printed by L-DED for load-bearing purposes (España et al. 2010). Although obtaining the certification for a printed implant from the National Medical Products Administration is a rather long and challenging process, these cases indicate great potential for metal powder-based AM technology to be utilized in manufacturing biomedical implants.

Patients with pelvic sarcomas typically require major bone grafts and implant installation after resectioning the cancerous tissue, but complex implant systems often fail shortly after being installed. For patients who have undergone major tissue removal, customized implants can be extremely beneficial since many large bone defects cannot be easily restored by standard implants. A case report has verified the clinical usage of a printed Ti–6Al–4V pelvic bone implant after removing a giant chondrosarcoma tumor (Chen et al. 2020). The implant possesses a porous structure to mitigate stress shielding (Figure 7.6a,b), and the patient achieved rapid recovery after the implant was installed (Figure 7.6c). No failure or loosening of the implant was observed 12 months after the patient began walking (Figure 7.6d).

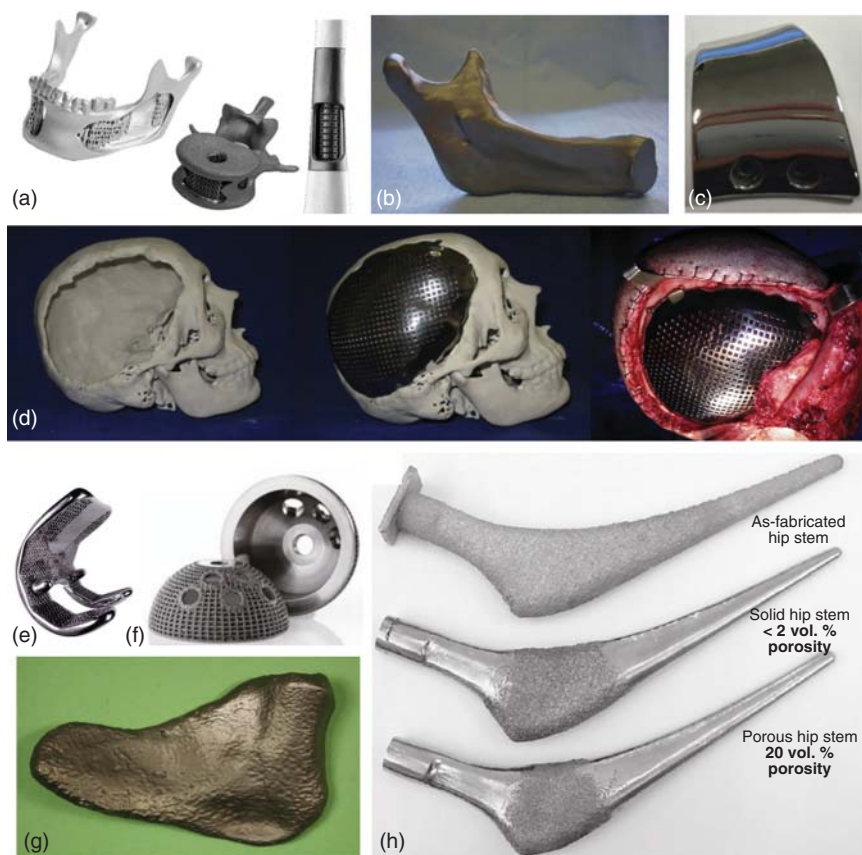


Figure 7.5 Implants fabricated by metal powder-based AM. Applications of LPBF. (a) Replacement mandible, lumbar vertebra, and tubular femoral bone. Source: Wehmöller et al. (2005)/reproduced with permission from Elsevier. (b) Mandible implant. Source: Bertol et al. (2010)/reproduced with permission from Elsevier. (c) Talar component. Source: Liverani et al. (2016)/reproduced with permission from Elsevier. (d) Frontoparietal-temporal bone. Source: Jardini et al. (2014)/reproduced with permission from Elsevier. Use of EBM: (e) Femoral knee implant. Source: Murr et al. (2012)/reproduced with permission from Elsevier. (f) Ti-6Al-4V acetabular cups. Source: Reproduced with permission from General Electric. (g) Skull plate. Source: Mazzoli et al. (2009)/reproduced with permission from Elsevier. (h) Hip stems with designed porosity values fabricated by L-DED. Source: España et al. (2010)/reproduced with permission from Elsevier.

With adherence to metal AM intraoperative guidelines and adequate preoperative planning, high-precision tumor removal can be conducted by most surgeons. Due to the anatomic variations in bone defects among different cancer patients who have undergone tumor removal, a highly personalized implant with soft tissue docks directly benefits their recovery. Printed metallic implants exhibit precise morphology that facilitates the attachment of muscles and ligaments, thereby increasing the stability of the implants and rendering it possible for cancer patients to achieve enhanced recovery after their surgery.

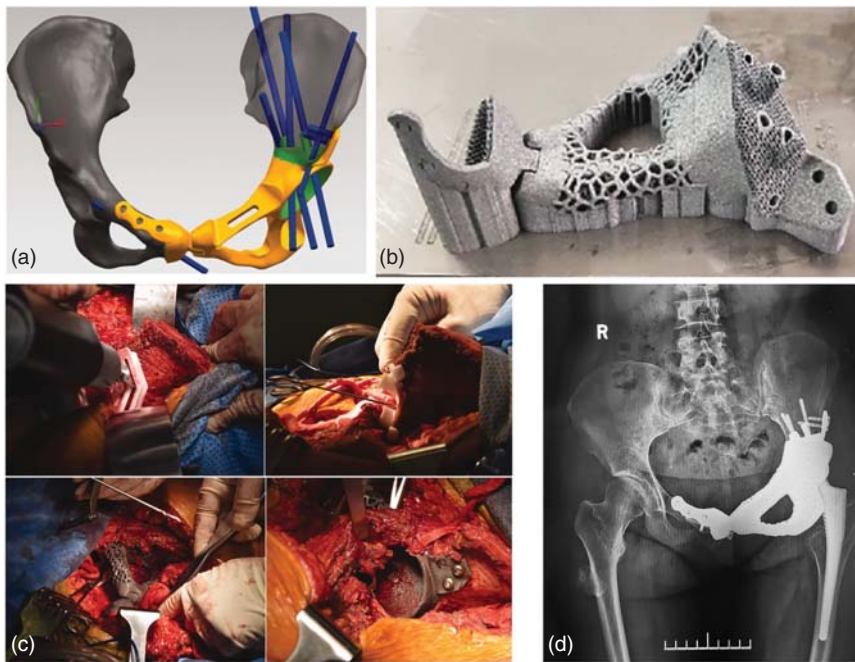


Figure 7.6 (a) Design of an implant model, (b) printed Ti–6Al–4 V implant, (c) surgical procedure of tumor resection and implant installation, and (d) computed tomography (CT) image indicating no failure or loosening of the implant 12 months after the surgery. Source: Chen et al. (2020)/reproduced with permission from SAGE Publications Inc., CC BY-NC 4.0.

Implant dentistry has improved the rehabilitation of edentulous patients, particularly individuals with alveolar bone resorption issues and poor reception toward conventional dentures. A variety of dental implants are available, but limitations on their designs and sizes may sometimes necessitate graft surgeries. The most common biocompatible dental materials are cobalt–chromium-based alloys, such as Co–Cr–Mo, Co–Cr, Co–Cr–Cu, and Co–Cr–W alloys, which have been established to fulfill the mechanical requirements of the ISO 22674:2006 standard with a yield stress of at least 500 MPa (Lu et al. 2015). A core issue that stems from such metallic implants is the release of metallic ions, which may result in diverse hypersensitivity or other undesirable tissue reactions for the patients. A previous *in vitro* study determined that in a simulated saliva environment and cell culture media, fewer Co ions were released from LPBF-printed samples than their cast counterparts (Xin et al. 2012). Co–Cr alloys manufactured via LPBF corresponded to higher cell proliferation and lower biological risks. Several companies, such as EOS, Concept Laser, and Renishaw, have utilized LPBF to produce copings for dental crowns and bridges, as shown in Figure 7.7.

Surface modification and coating are effective approaches for enhancing osseointegration between living tissue and metallic implants. Calcium phosphate ceramic is the most popular coating material for metallic implants, and calcium phosphate

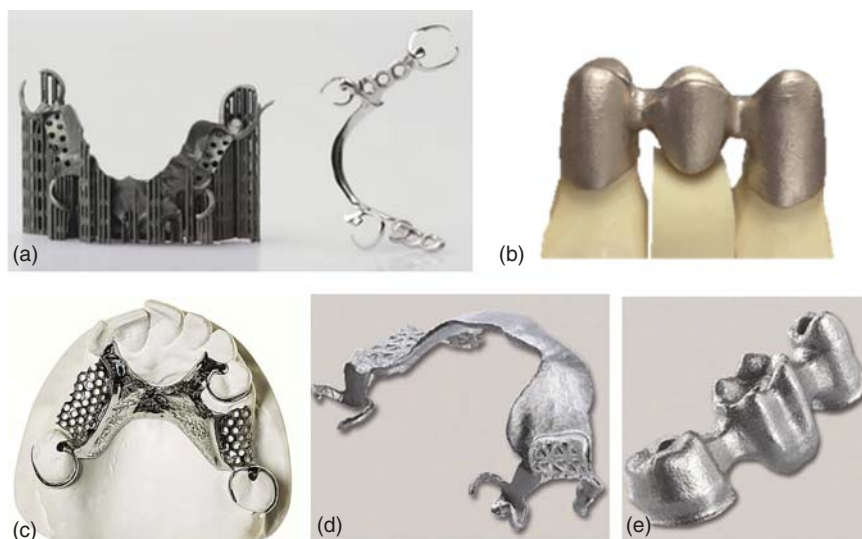


Figure 7.7 Dental implants fabricated by LPBF. (a) Co-Cr removable partial denture with supporting structures after manufacturing and the final product with a polished surface and (b) Dental bridge. Source: Reproduced with permission from EOS. (c) Removable partial denture. Source: Reproduced with permission from Renishaw plc. (d) Ti-6Al-4V dental prosthesis and (e) Co-Cr dental bridge. Source: Reproduced with permission from General Electric.

coatings with graded composition and a controlled porosity can be manufactured through L-DED to boost their biocompatibility and improve osseointegration (Bose et al. 2018). Metallic implants and bioceramic coatings can be simultaneously processed through L-DED. A widely studied bioactive coating material, hydroxyapatite, has been determined to improve the biological inertness of pure titanium (Han et al. 2017a; Han et al. 2018a). Electrophoretic deposition is a liquid-based method with a short processing time. It requires only simple equipment, provides easy control of parameters, and boasts a wide range of possible coating materials. Such materials have been explored to design novel coatings for metallic porous structures (Han et al. 2017c). Specifically, a gentamicin-loaded silk fibroin coating with a thickness of $2.3\mu\text{m}$ was successfully prepared and adsorbed onto LPBF-printed porous Co-Cr-Mo bone substitutes through process optimization, which enhanced the initial osteoblastic response of the implants and suppressed bacterial activity.

The development of metal powder-based AM techniques within the biomedical industry is predicted to continue in the foreseeable future due to their ability to align with in-demand medical device components. Most medical devices, such as dental crowns and surgical implants, require miniaturization, and hence AM techniques are highly applicable for fabricating such equipment. Additionally, these techniques can achieve clinical efficacy, for which the as-produced medical components can be specifically tailored to each patient and exhibit excellent

properties. Meanwhile, metal powder-based AM companies are also introducing advanced machines for processing metal products rapidly and cost-effectively.

7.3 Automotive

The automotive industry is one of the most competitive business domains, in which a decrease in production time and time to market grants a massive advantage over fellow competitors. Driven by novel design trends and technological evolution, of which esthetics, aerodynamics, safety, and vehicle weight reduction are critical issues, automotive companies are developing new models and innovative measures daily. Metal powder-based AM has been utilized as an important tool in the design and development of small quantities of structural and functional automotive components, such as engine exhausts, driving shafts, gearbox components, and braking systems for low-volume luxury automobiles. Such extensive application of AM can be attributed to its ability to shorten the development cycle and reduce production costs. However, AM is currently only employed for prototyping and the direct manufacturing of non-safety-relevant components in small batches, mainly because the process reliability and consistency of AM are still limited.

Companies and research institutes have successfully applied AM techniques to manufacture functional components for motorsport vehicles. These usually comprise lightweight alloys (e.g. titanium) and possess highly complex structures and low production volumes. For example, CRP Technology of Italy has successfully applied LPBF and EBM to develop various components for motorsports, including Formula One (F1) titanium gearboxes, MotoGP 250R air boxes, motorbike dashboards and supports, camshaft covers for MotoGP engines, reed valves, F1 suspension systems, etc. Compared to their conventionally manufactured counterparts, F1 gearboxes fabricated through AM were approximately 20–25% lighter and 20% more compact while possessing twice the torsion stiffness with minor gear wear and power absorption. For example, the steering knuckle of a race car, which was fabricated by EOS via LPBF, is shown in Figure 7.8a. The weight of the printed steering knuckle was reduced by 35%, and its stiffness was improved by 20% compared to its conventionally manufactured counterpart.

Optomec manufactured a Ti–6Al–4V suspension mounting bracket (Figure 7.8b) and driving shaft spiders for a Red Bull race car through L-DED, achieving a material reduction of over 90% and significantly lowering the production time and cost. Arcam applied EBM to produce Ti–6Al–4V components for race cars, such as gearboxes (Figure 7.8c), suspension parts, and engine parts with lattice structures (Figure 7.8d). Concept Laser has produced steel and aluminum automotive components via LPBF, which include wheel suspension systems, oil pump housing units (Figure 7.8e), engine blocks, exhaust manifolds (Figure 7.8f), and valve blocks. A water pump for motorsports cars was also fabricated through LPBF using Al–Si10–Mg (Figure 7.8g). It exhibited mechanical properties comparable to its conventionally heat-treated counterparts (Vilaro et al. 2008).

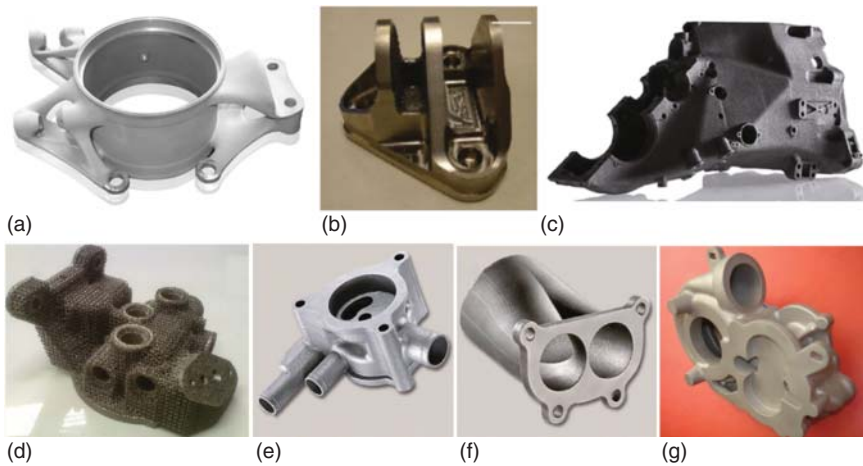


Figure 7.8 (a) Race car steering knuckle produced by LPBF. Source: Reproduced with permission from EOS. (b) Suspension mounting bracket for a Red Bull race car produced through L-DED. Source: Reproduced with permission from Optomec, Inc. (c) Race car gearbox and (d) Ti-6Al-4V engine component with lattice structures fabricated through EBM. (e) Oil pump housing unit and (f) exhaust manifold produced through LPBF. Source: Reproduced with permission from General Electric. (g) Water pump unit for a motorsports car produced through LPBF. Source: Vilaro et al. (2008)/reproduced with permission from European Forum.

Delphi, a top-tier automotive supplier, employs LPBF instead of traditional machining to fabricate diesel pumps. The LPBF process allows the pumps to be manufactured as single units. It bypasses several operations, such as drilling, machining, and chemical deburring, thereby reducing the overall production costs and yielding a final product less prone to leakage. Conventional gravity-casting and machining processes for producing pump housing units typically require a buy-to-fly ratio of 2 : 1. But with LPBF, a significantly lower buy-to-fly ratio of 1.4 : 1 can be achieved for the same units.

Extensive efforts on material development in the automotive industry have been expended. For instance, EOS Maraging Steel MS1 developed by EOS GmbH has a chemical composition similar to that of 1.2709 steel (X3NiCoMoTi 18-9-5), and it provides a viable alternative to the latter in the production of conventional tool inserts. Meanwhile, a TiAl alloy with low density, high specific strength (ratio of elastic modulus to density), and high stiffness (ratio of yield strength to density) designated for EBM has been adopted for fabricating automotive engine components (e.g. engine exhaust valves and pistons) (Murr et al. 2010).

While the rapid prototyping of functional test components remains a highly attractive feature of metal powder-based AM, the production of specialized parts is also actively pursued (e.g. parts involved in vintage automotive restoration). The mass production of automotive components poses a huge challenge for the aforementioned printing processes, i.e. EBM and LPBF. However, small-scale production of automotive metal parts can be easily achieved. In particular, printing a mold from sand or plastic through binder jetting followed by casting is a popular method, and casting large complex parts through such molds can reduce the development time,

allowing for multiple design iterations during the prototyping phase. Notably, ExOne produced a batch of five castings from AM molds at €1500 per unit cost. In contrast, conventional patterns, tools, and lost foam casting methods could cost up to €15 000–20 000.

7.4 Molding and Tooling

Metal powder-based AM processes have been employed to manufacture highly geometrically complex molds and tools. Such processes can produce mass-production molds and tools containing 3D conformal cooling channels, which are difficult to fabricate through conventional processes (casting, machining, forging, etc.) and must meet stringent requirements with respect to their properties (hardness, wear resistance, strength, heat conduction, etc.) and service life.

The cooling of parts in molds is the most time-consuming phase of the plastic injection molding process. A decrease in the cooling time boosts the production rate, produces molded parts of higher quality, and reduces wastage. Various conventional techniques, such as implementing bubbler cooling systems and heat pipes and performing complex drilling operations using laminated blocks, have been utilized to maintain a uniform temperature during the cooling process, which is usually tedious and inefficient. Conventional cooling channels are commonly machined in straight lines, rendering them unable to facilitate reliable cooling across a mold cavity due to non-uniform heat conduction. Inhomogeneous cooling results in long cycle durations, warpage, and possible scrapping of the final parts. Conformal cooling molds possess curved cooling channels that align closely with the overall geometry or contours of the mold, thereby maintaining a uniform temperature throughout the structure. While conformal cooling solutions can significantly reduce the total production cost by decreasing the mold cycle time, they typically require sophisticated individual mold designs that constitute a wide variety of unconventional curves, twists, and shapes that must be precisely implemented.

The design and fabrication freedom of metal powder-based AM techniques spurs the application of conformal cooling channels in the molding and tooling industries. Compared to conventional processes, utilizing such techniques can realize complex contour designs on the surface of a mold, particularly for molds with multiple cavities, which are utilized in the areas of injection molding, die casting, blow molding, hot extrusion, and hot stamping (Shinde and Ashtankar 2017). Additionally, AM can be employed to repair or modify existing tools and extend the lifespan or improve the performance of these products.

Presently, LPBF is the most popular metal powder-based AM process for printing molds and tools. Numerous commercial companies have been exploring the applicability of AM in manufacturing geometrically complex molds containing conformal cooling channels (Figure 7.9). For example, B&J Specialty, Inc. utilized a Prox DMP 300 machine developed by 3D Systems to produce a mold containing specialized inner cooling channels optimized through numerical simulations (Figure 7.9b). The printed product corresponded to a reduction in cycle cooling time from 1 minute to 40 seconds, an 86% reduction in temperature variation during cooling, an increased

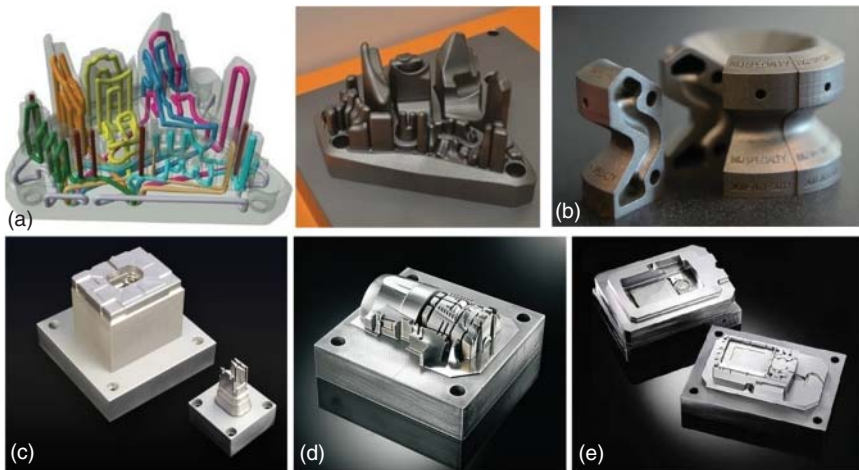


Figure 7.9 Mold products printed through LPBF by commercial companies. (a) Mold with eight complex conformal cooling channels. Source: Reproduced with permission from Renishaw plc. (b) Mold with inner cooling channels optimized through numerical modeling. Source: Reproduced with permission from B&J Specialty, Inc. Molds printed using a hybrid metal 3D printer for (c) waterproof connector, (d) electric driver, and (e) digital camera. Source: Reproduced with permission from Matsuura Machinery Corporation.

mold lifetime, and the delivery of higher-quality parts, thereby decreasing the production time and costs for tool manufacturers and mold operators. Employing a machine-aided LPBF strategy, Matsuura Machinery Corporation printed molds for a waterproof connector, an electric driver, and a digital camera through a hybrid metal 3D printer using Matsuura Maraging II powder (Figure 7.9c–e). The hybrid-manufactured molds have significantly improved surface quality compared to those printed without machining.

The installation of complex conformal cooling channels within mold inserts expedites the molding process and improves the quality of the products. Figure 7.10a presents a finished and polished mold insert with complex cooling channels, which was printed through LPBF by GPI Prototype and Manufacturing Services. The printing process lasted about 39 hours and costs US\$3300. The printed mold insert was still in use after 190 000 shots. Oskar Frech GmbH initiated industrial-scale AM over a decade ago and introduced the first Frech Gating System distributors for branch gate die casting in 2007. The main applications of AM in die casting include the fabrication of distributors, prototypes, and inserts for die-casting molds capable of facilitating conformal cooling. With an SLM280 machine, Frech primarily used an aluminum alloy and a tool steel 1.2709 to produce prototypes and inserts for die-casting molds containing complex conformal cooling channels, respectively (Figure 7.10b), which provides a novel and efficient approach for tempering cores, wipers, and even anvils. A cooling time reduction of about 60% was achieved for the printed mold, and the total process cycle time was shortened by 12% consequently. Through LPBF, Additive MFG implemented conformal cooling channels within

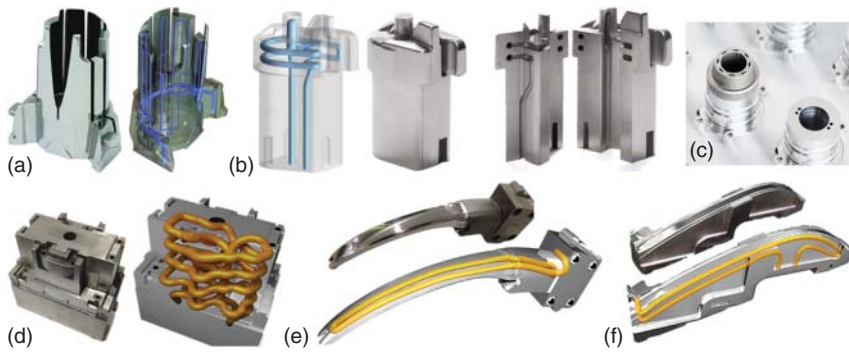


Figure 7.10 Mold inserts with conformal cooling channels printed via LPBF. (a) finished and polished mold. Source: Reproduced with permission from GPI Prototype and Manufacturing Services. (b) Printed mold that could achieve a reduction of about 60% in its cooling time. Source: Reproduced with permission from SLM Solutions. (c) Printed molds with different channels. Source: Reproduced with permission from EOS. Mold inserts for different applications. (d) Contactor bracket, (e) car handle, and (f) car light lens. Source: Reproduced with permission from General Electric.

mold inserts for contactor brackets, car handles, and car light lenses while partnering with Schneider Electric, Volkswagen, and DS Automobiles, respectively. Figure 7.10c–f display these products, which were printed using an EOS M 290 printer. The quality of the injection parts was tremendously improved compared to their conventionally manufactured counterparts.

Conventional tool production processes reach their limitations where the tempering channels can only be drilled in straight lines, which often results in coolants being unable to reach critical hotspots. As a result, the tool may become deformed, and its service life will be reduced. Additionally, partially deficient heat dissipation is responsible for a long cooling time. LPBF powder materials suitable for hot stamping tooling are maraging steels, CL50WS, EOS Stainless Steel CX, and H13 (Chantzis et al. 2020). LBC Laser Bearbeitungs Center GmbH designed and manufactured a tool insert with a significantly optimized tempering performance using an EOS-developed Maraging Steel MS1 powder for the die casting process. During manufacturing, tempering channels were integrated into the tool at defined points, thereby significantly improving its cooling performance and achieving a 20% reduction in its cycle time. A few typical tooling inserts printed through LPBF are shown in Figure 7.11.

Fraunhofer ILT has combined the advantages of conformal cooling channels with the excellent heat conductivity of copper and implemented them within a tool, as shown in Figure 7.11d, thereby reducing its cycle time and minimizing warpage. SLM Solutions also reduced the cycle time of an injection molding tool from 60.5 to 14.7 s by optimizing its conformal cooling insert (Figure 7.11e). Additionally, the cooling time was reduced by about six seconds.

A comparison between AM and conventional manufacturing procedures provides suitable indicators for the future process selection for tool fabrication. For example, in the automotive stamping industry, blank inserts are typically laminated and cut to

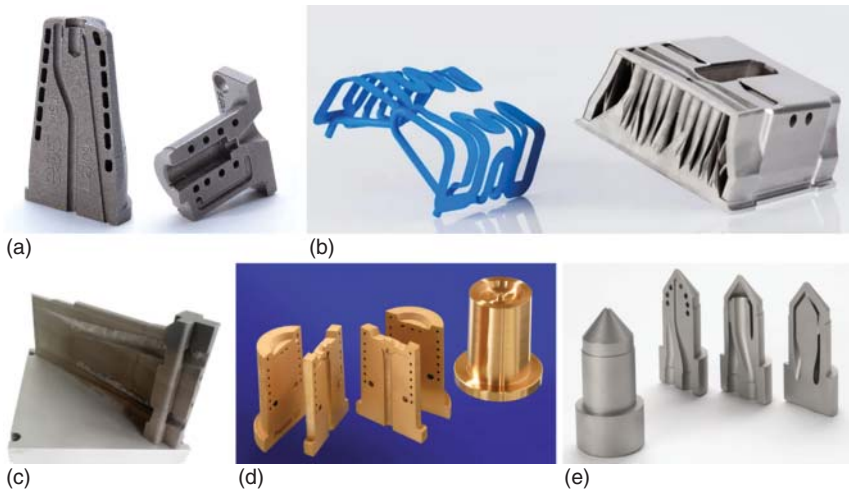


Figure 7.11 Tool inserts printed via LPBF. (a) Printed inserts for die casting, (b) lightweight Audi Hotforming Tool insert with conformal cooling channels, and (c) automotive armrest. Source: Reproduced with permission from EOS. (d) Inserts printed using Hovadur K220. Source: Reproduced with permission from Fraunhofer ILT. (e) Injection molding tool inserts after channel optimization. Source: Reproduced with permission from SLM Solutions.

a near-net shape before undergoing heat treatment to obtain the required properties. Subsequently, the desired surface quality and final tolerance are achieved through proper surface finishing. Meanwhile, tool inserts may be produced through casting processes employing pre-manufactured lost foam models, which may require outsourcing and significantly increase the final tooling lead time. The utilization of LPBF to fabricate cutting tools has been proven to shorten the lead time (Leal et al. 2017). In addition, despite its relatively high processing costs, cost breakdown analyses have indicated that LPBF requires substantially fewer operations than the lost foam process, thereby simplifying the internal logistics.

The cooling performance of an EBM-printed H13 tool insert with conformal cooling channels was found to be superior to that of its traditionally machined counterpart with straight cooling channels (Rännar et al. 2007), which boosts the productivity and the dimensional accuracy of the final products. However, because of a relatively large beam spot size, the EBM process encounters difficulties in printing parts featuring a small radius. Therefore, the shape and dimensions of the cross section of a cooling channel should be considered and optimized before fabricating it via EBM.

In addition to the direct fabrication of molds, tools, and tool inserts, another significant application of AM constitutes the repair and remanufacturing of such instruments. Compared to traditional repair techniques (e.g. tungsten inert gas/plasma and gas tungsten arc welding), L-DED is capable of providing precise, small deposits with good metallurgical properties through a focused and highly concentrated laser beam. For example, a CPM 9V steel powder was selected to repair the surface of a H13 tool steel plate through L-DED (Kattire et al. 2015), and compressive residual stress was present within the plate, which impeded crack propagation and increased

its service life. In addition, a Ni–Co–Mo alloy has been developed as part of a fast, efficient, and cost-effective repair strategy for worn surfaces of maraging steel molds (Grum and Slabe 2004), which increases their durability.

7.5 Energy

Efficient energy conversion, transmission, and storage are the ultimate goals of the energy industry. Therefore, manufacturing methods that can precisely transform materials into functional and efficient energy conversion and storage devices are of paramount importance. AM can reduce the cost and lead time of new products through the rapid development and fabrication of prototypes. In particular, AM can be employed to fabricate compact energy-saving devices with a high surface area, such as heat exchangers. Current applications of metal powder-based AM in the energy sector mostly fall within the domains of thermal energy conversion and production of fuel cells and chemical reactors for energy and fuel processing.

Heat exchangers, which typically exhibit complex geometries that include thin walls and complex fluid passages to achieve efficient heat transfer with a low pressure drop along the flow paths, are commonly fabricated through metal powder-based AM processes. Traditionally manufactured heat exchangers typically comprise brazed pieces of sheet metal with a low yield of parts and limited geometrical complexity. In contrast, AM heat exchangers are lightweight and space-efficient non-assembly systems with increased surface areas. Additionally, they possess welded seams that eliminate the risk of leakage and complex-shaped internal channels for optimized coolant flow and functional integration.

Enhancing the heat transfer performance of heat exchanger products, particularly through miniaturization, is a major research topic in the energy industry. Figure 7.12 displays common commercial heat exchanger products fabricated via AM. Conflux Technology, an Australian company specializing in thermal and fluid dynamic solutions, has introduced a novel heat exchanger designated for AM, namely, the Conflux Core™ heat exchanger (Figure 7.12a). This heat exchanger design has been employed in the automotive and oil and gas industries, as well as in chemical process technologies. The printed heat exchanger is 22% lighter than its conventionally produced counterparts and can dissipate thrice the amount of heat in a given time. Using EOSINT M 280 printers, the Betatype company fabricated heat sink units for automotive LED lights (Figure 7.12b). A total of 384 parts were manufactured in a single batch, and the optimized part design and precise laser scanning paths reduced the production time from 444 hours to only 34 hours. In addition, the unit costs were reduced by 90%. EOS developed a passive heat exchanger with a unique shape resembling a sea anemone that maximizes its surface area (Figure 7.12c).

Velo3D developed a radio flow heat exchanger (Figure 12d) and a diamond heat exchanger (Figure 7.12e) through their unique support-free LPBF technique, which greatly increases the design freedom of complex parts and improves their printability. In collaboration with SLM Solutions, URMA AG successfully employed

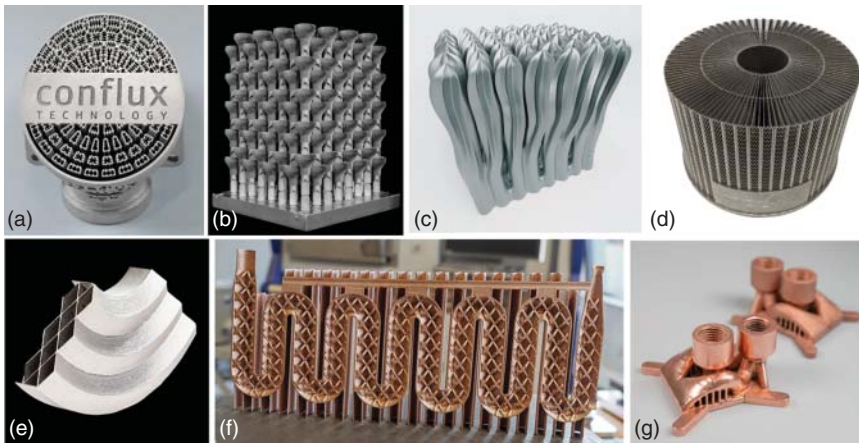


Figure 7.12 Heat exchangers printed through LPBF by commercial companies. (a) Conflux Core heat exchanger, (b) single batch of 384 heat sinks produced by Betatype, and (c) an EOS Corel aluminum heat sink. Source: Reproduced with permission from EOS. (d) Diamond heat exchanger, and (e) radio flow heat exchanger. Source: Reproduced with permission from Velo3D. (f) Copper heat exchanger. Source: Reproduced with permission from URMA AG. (g) LPBF-printed gaming CPU cooler. Source: Reproduced with permission from EOS.

LPBF to fabricate a copper heat exchanger (Figure 7.12f). A complex assembly of parts with different functions was integrated into a single unit that displayed improved heat transfer performance and a low pressure drop. Such freedom in design reveals the potential of AM in optimizing heat exchanger devices with respect to their mechanical integrity, heat transfer performance, and flow behavior.

Imperfect heat dissipation limits the miniaturization of portable computers, electronic devices, and high-power lights. AM can mitigate such a restriction by fabricating thermal management components that dissipate heat efficiently, even in confined regions. In addition, the freedom of design incorporated within AM components may render their thermal management performance superior to that of conventionally manufactured components, often with lower space requirements. For example, EOS and AM Metals GmbH have pushed the limits of AM and developed a state-of-the-art gaming central processing unit (CPU) heat exchanger designated for LPBF (Figure 7.12g). AM Metals manufactured a water-cooled heat exchanger through a flexible EOS M 290 system. The LPBF-printed CPU cooler exhibits a cooling capacity similar to those of other high-end gaming CPU coolers despite being just one-fifth of their size and a quarter of their weight.

Aside from industrial companies, researchers in academia have also made efforts to improve the fabrication of heat exchangers and their applications. For example, a pitot tube incorporated with heat sinks was printed using an Al-Si-Mg powder via LPBF, which achieved a 98% improvement in heat transfer compared to conventional heat sinks (Fasano et al. 2016). Figure 7.13a–c present different designs for printed aluminum heat sinks, namely, Pinfin-Al6061 with a conventional geometry, V-Al6061, which comprises angled ellipses, and Diamond-Al6061, which

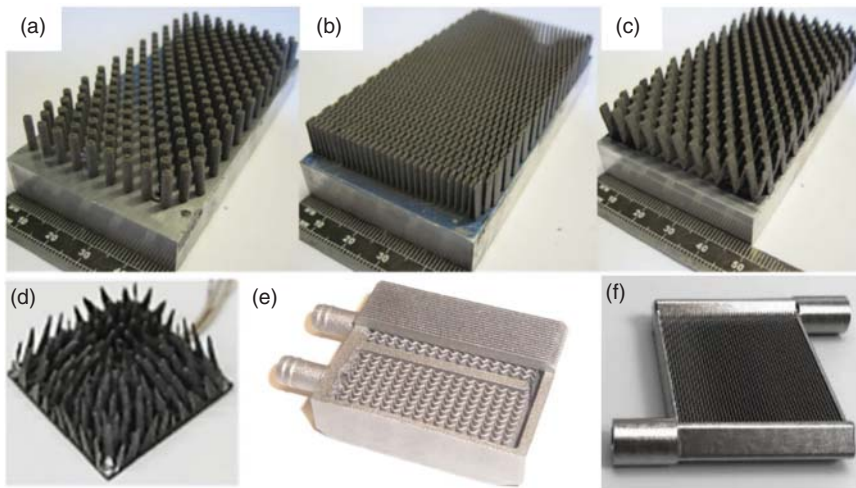


Figure 7.13 Heat sinks fabricated through LPBF. (a) Pinfin-Al6061, (b) Diamond-Al6061, and (c) V-Al6061. Source: Wong et al. (2007)/reproduced with permission from Emerald Publishing Limited. (d) Printed AlSi12 component with a novel design. Source: Dede et al. (2015)/reproduced with permission from American Society of Mechanical Engineers. (e) Compact cooler unit with extremely intricate inner geometry fabricated through LPBF using copper. Source: Neugebauer et al. (2011)/reproduced with permission from Emerald Publishing Limited. (f) Miniaturized air-to-refrigerant heat exchanger prototype fabricated through LPBF. Source: Reproduced with permission from The University of Maryland. Center for Environmental Energy Engineering.

is composed of diamond-shaped pins (Wong et al. 2007). Both the Diamond-Al6061 and V-Al6061 designs cannot be realized through conventional manufacturing methods because of their unique geometrical properties. In particular, Diamond-Al6061 exhibited a tremendous improvement in heat exchange due to its complex fins possessing a large surface area.

The capability of LPBF to fabricate complex 3D heat sink designs was further validated by Wong et al. (2009). They demonstrated that the heat transfer performance of printed heat sinks could be determined mainly by the path of the coolant. Figure 7.13d shows a novel heat sink fabricated through LPBF using AlSi12 powder (Dede et al. 2015). Confined jet cooling tests indicated that the printed novel heat sink design possessed a relatively high coefficient of performance, which can be attributed to a lower jet flow resistance due to its unique blended fin design. Figure 7.13e presents a compact cooler unit fabricated through LPBF with a highly complex inner geometry (Neugebauer et al. 2011). The cooler ($46 \times 59 \times 15 \text{ mm}^3$) includes a large number of cooling fins, each with a thickness of 0.3 mm, to facilitate efficient heat exchange. A high surface-to-volume ratio and rapid coolant flow were achieved by modifying the rib-like internal structure of the unit. Intending to develop a new generation of compact, highly efficient heat exchangers, researchers from the University of Maryland designed and produced a miniaturized 1 kW air-to-refrigerant heat exchanger prototype through LPBF (Figure 7.13f), which was 20% lighter and 25% more energy-efficient than its conventionally

manufactured counterparts. In addition, the fabrication process was shortened from months to weeks.

High-pressure reactors are employed in process engineering for facilitating chemical reactions under pressure values of below 200 bar. Traditionally, such reactors are built from stainless steel or Hastelloy. In a collaborative endeavor between THALETEC GmbH and the engineering office JUREC, a prototype of a high-pressure reactor was developed and fabricated using an SLM280 machine. LPBF allows a temperature control channel to be integrated within the reactor, which significantly improves heat transfer between its interior and the temperature control fluid. In addition, compared to traditional reactors, the LPBF-printed reactor could accommodate a high pressure before succumbing to damage, and its weight is lower due to its optimized thinner wall design.

In the design of energy systems, chemical and geometrical control on small scales are of great importance. Although the majority of established metal powder-based AM techniques are unable to reach the realm of nanofabrication, their advantages over conventional manufacturing methods and capability to fabricate active materials and functional microstructures have rendered them excellent candidates for applications within fuel-processing chemical reactors. A steel dehydrogenation reactor exhibiting a cubic diamond cellular structure was fabricated through EBM using Ti-6Al-4V powder, as shown in Figure 7.14a (Peters et al. 2015). The optimized cellular structure was determined to enhance the cooling performance of the reactor and facilitate efficient hydrogen gas removal from the surface of the catalysts. Ten reactors were scaled up to form a single hydrogen release unit, and a H_2 generation rate of 9.8 NL/min was achieved. Figure 7.14b shows a novel EBM-printed 3D catalyst support structure employed in catalytic static mixers for hydrogenation reactions (Avril et al. 2017). Catalytic static mixers are derived from static mixer concepts, in which a geometrically optimized mixer is coated with a catalyst and fitted within a tubular flow reactor, as shown in the diagram. Presently, all catalytic static mixers are produced through a combination of EBM and other metal deposition techniques.

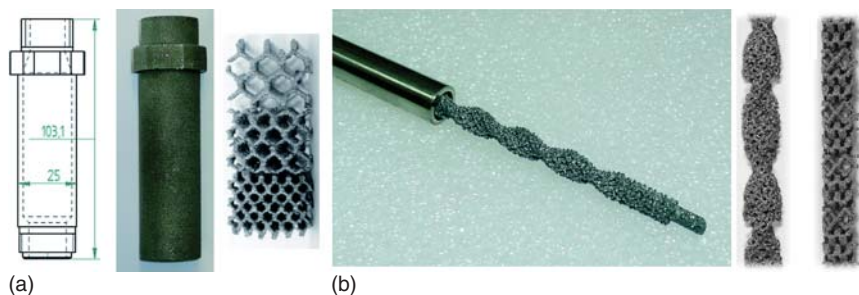


Figure 7.14 Chemical reactor components printed through EBM. (a) Reactor tube with a diamond-shaped porous internal structure. Source: Peters et al. (2015)/reproduced with permission from Royal Society of Chemistry. (b) Support structures of different designs in catalytic static mixers. Source: Avril et al. (2017)/reproduced with permission from Royal Society of Chemistry.

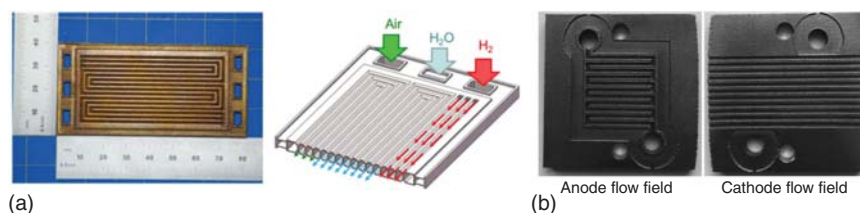


Figure 7.15 Fuel cell components printed through LPBF. (a) Ti-6Al-4V BPP and a sectional view of a BPP solid model with triple serpentine flow fields and straight, parallel internal coolant channels. Source: Gould et al. (2015)/reproduced with permission from The Electrochemical Society. (b) 316L stainless steel BPPs at the anode and cathode of a PEMFC. Source: Dawson et al. (2015)/reproduced with permission from Springer Nature.

Metal powder-based AM can be potentially utilized to manufacture microbial fuel cells as single units. This possibility was explored by using LPBF to manufacture a bio-inspired lattice aluminum alloy anode to improve the functionality of microbial fuel cells, which resulted in a higher power density than other metallic anodes (Calignano et al. 2015). Furthermore, the LPBF-printed anode possessed a 3D macroporous structure with ideal properties for hosting anodophiles, such as low density, large specific surface area, and customizable surface roughness. The cellular lattice structure of the anode resulted in better microbial attachment, enhanced charge transfer between anodophiles and the electrode surface, and facilitated rapid nutrient diffusion without clogging.

Metal bipolar plates (BPPs) are speculated to provide a path to developing a low-cost, compact fuel cell stack (Netwall et al. 2013). As shown in Figure 7.15a, LPBF was employed to print BPPs from a Ti-6Al-4V powder, which were subsequently coated with a low-cost, robust, conductive TiO₂/gold composite to improve their corrosion resistance and minimize their surface resistance (Gould et al. 2015). A single proton-exchange membrane fuel cell (PEMFC) stack comprising two printed BPPs achieved similar fuel efficiency to conventionally manufactured carbon BPPs. One of the largest contributions to the overall cell resistance is the contact resistance originating from the interfaces between the gas diffusion layer and the BPPs. In another study that demonstrates the applicability of LPBF in printing 316L stainless steel BPPs for PEMFCs (Dawson et al. 2015), the interfacial contact resistance and overall fuel efficiency of the PEMFCs containing the printed BPPs were determined to be on par with those of other PEMFCs utilizing conventionally fabricated BPPs, as shown in Figure 7.15b.

7.6 Jewelry

Consumers are influenced by the rapidly advancing digital revolution to expect a continuous and regularly updated selection of innovative products, particularly jewelry. Furthermore, an ever-increasing number of consumers are interested in the unique personalized designs of jewelry pieces. Thus, the future of the high-value

jewelry market could well depend on the growing demand for individual and innovative representations of high-quality jewelry products.

While all materials involved in producing precious metal jewelry are inherently expensive, metal powder-based AM (particularly LPBF) introduces a technology shift that can potentially reduce material usage while facilitating the fabrication of uniquely designed, high-value, and personalized jewelry products. In addition to the fabrication of jewelry from stainless steel, titanium-based alloys, nickel-based alloys, aluminum, and copper (Yap and Yeong 2014), LPBF has also been employed to manufacture products composed of precious metals, including 18-karat gold of various colors, silver alloys, and platinum group metals. Notably, rings, bracelets, necklaces, and pendants of complex designs can be printed through LPBF (Yap and Yeong 2014). Cooksongold AM, a division of Cookson Precious Metals Ltd. and Sempsa JP, is a leading company in printing precious metals, having collaborated with EOS to produce gold jewelry products through a specialized LPBF machine. The structures of these products can be modified to accommodate cavities, corresponding to lighter weight and allowing for unique design choices. Figure 7.16 presents an assortment of LPBF-printed gold jewelry pieces from Cookson Precious Metals and Cooksongold.

Flexible joining mechanisms can be incorporated within a design to render it foldable. These mechanisms are composed of multiple small components that interlock at accurately spaced hinge joints, thereby enabling the overall structure to drape and move in a manner akin to that of actual fabric. Such designs are implemented in flexible and customizable bracelets and necklaces.

The visual esthetics of a product is an essential indicator of its value. Thus, the visual appeal of printed fashion products should be on par with that of their traditionally manufactured counterparts. Post-processing of printed jewelry is required since they are typically unattractive otherwise (Figure 7.17a–c) (Klotz et al. 2016). Generally, manual polishing, a time-consuming and costly process, must be performed on printed jewelry instead of mechanical methods to provide it with an intricate and complex surface. Afterward, electroplating or anodizing can be conducted on the jewelry pieces to enhance their esthetics and durability further. Electroplating procedures, such as chrome plating, can be performed on the surface of both polymer and metal components, while anodizing is only applicable to metals. The former can reproduce the appearance and texture of a



Figure 7.16 (a) Cufflinks and (b) a ring are made of 18-karat yellow gold. Source: Reproduced with permission from Cookson Precious Metals Ltd. (c) Sculpture and (d) galleon are both printed in gold. Source: Reproduced with permission from Cookson Precious Metals Ltd.

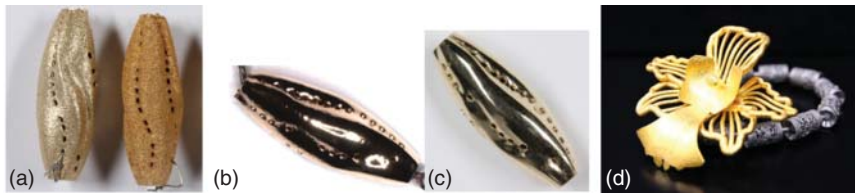


Figure 7.17 Jewelry samples printed by LPBF using 18-karat yellow gold with different polishing steps. (a) As-printed (left) and sand-blasted (right), (b) electro-polished, and (c) hand-polished samples. Source: Klotz et al. (2016)/reproduced with permission from Santa Fe Symposium. (d) “Orchid-Spirit” dual-function bracelet manufactured by LPBF using Ti-6Al-4V and anodized to form gold flower petals. Source: Yap and Yeong (2014)/reproduced with permission from Taylor & Francis Group.

metallic coating and enhance the wear resistance of a component. In contrast, the latter allows the component to be dyed in a variety of colors. Interestingly, different colors of anodized titanium can be obtained simply by varying the thickness of the oxide layer, and no dye is involved. Figure 7.17d shows an anodized “Orchid-Spirit” golden titanium bracelet fabricated through LPBF (Yap and Yeong 2014).

7.7 Marine, Oil, and Gas

The marine, oil, and gas industries have been much slower to embrace metal powder-based AM than the aforementioned industries. The rapid prototyping of tools and complex models, which allows multiple design cycles and quick testing of design concepts, is particularly significant in the oil and gas industries.

Using LPBF has reduced the product development time of a burner for a NovaLT16 gas turbine through rapid prototyping of design concepts and accelerated validation testing, thereby resulting in a cost reduction of over 50%. In addition, compared to investment casting, AM allows for the simplified manufacturing of pumps, turbomachinery, valves, and other vital components, which reduces costs and enhances the mechanical performance of the products. Specifically, GE Oil & Gas Additive Manufacturing Laboratory has installed multiple LPBF machines to fabricate turbomachinery components.

The supply chain management sector in the oil and gas industries may benefit more from the advantages of AM than improvements in part performance and reduction in the production cost (Holmström et al. 2010). With oil and gas assets being deployed in isolated regions for increasingly longer durations, essential components are more likely to break down, become obsolete due to technological changes, undergo changes in quality, or go out of production. Through AM, obsolete components can be reverse-engineered digitally and manufactured on demand, leading to longer asset lifetimes.

As the pursuit of new reserves assigns oil companies to relatively remote locations, the prospect of on-site manufacturing becomes increasingly alluring. Many drilling rig components include multiple parts that must be welded, bolted, or brazed, and

fabricating single parts at remote locations through AM to replace their faulty counterparts can significantly reduce the cost and downtime. Rotterdam Additive Manufacturing Lab has pioneered a combined usage of robotic arm wire-arc AM and CNC milling to manufacture a 400 kg triple-bladed propeller prototype from a corrosion-resistant nickel–aluminum–bronze alloy, which was established as the world’s first approved AM ship propeller. Such innovation paves the way for the rapid fabrication of replacement parts for ships worldwide without requiring the parts to be ordered, remotely manufactured, and delivered. Subsequently, the printability of the nickel–aluminum–bronze alloy and its multi-material parts through L-DED was investigated for marine and offshore applications (Li et al. 2021, 2022). However, further applications of metal powder–based AM in the industry should still be explored.

Metal powder–based AM techniques are employed by the maritime and marine & offshore sectors for (i) improving the manufacturing process of complex spare parts; (ii) rapid prototyping of parts for installations or retrofitting projects; (iii) replicating the scales of ships, rigs, or equipment models with detailed features; (iv) smoothening workflow and planning; (v) speeding up performance testing; (vi) minimizing errors in new product development; and (vii) reducing storage space and related costs with on-demand local printing.

Researchers from the Singapore Centre for 3D Printing at Nanyang Technological University have utilized EBM in an offshore wind turbine project to fabricate a Pelton turbine system that can harvest renewable hydroelectric energy, which includes a Pelton wheel with an outer diameter of ~210 mm, a penstock, a nozzle, and a regulator (Figure 7.18). Ti–6Al–4V powder was selected to manufacture the turbine wheel because of its excellent corrosion resistance and mechanical strength. Compared to its original counterpart designated for conventional manufacturing, the total part count of the EBM-printed turbine system was reduced from 40 to 3, with a total weight reduction of about 40%. A complete EBM-printed Pelton turbine system containing such non-assembly components can reduce the cost from S\$90 000 to S\$9000 and the production cycle from six months to two weeks.

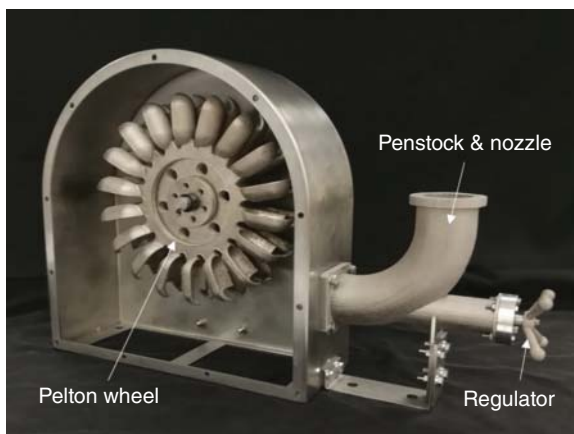


Figure 7.18 EBM-printed Pelton turbine system including a Pelton wheel, penstock, nozzle, and regulator for harvesting renewable hydroelectric energy. Source: Reproduced with permission from Nanyang Technological University.

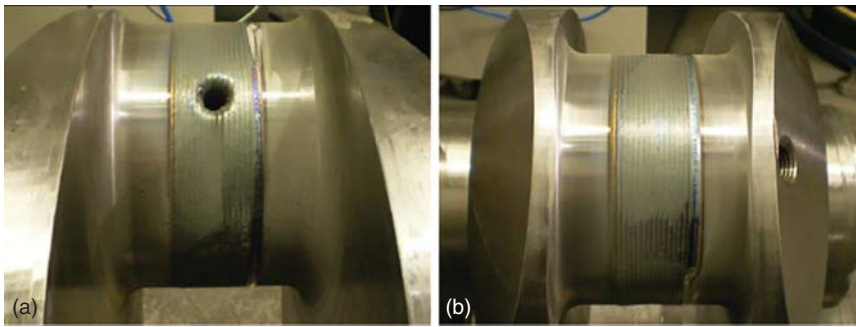


Figure 7.19 Crankshaft repaired by L-DED. (a) Oil-bore region and (b) its bottom side at the lower dead center position. Source: Koehler et al. (2010)/reproduced with permission from Elsevier, CC BY-NC-ND 3.0.

Diesel engines have undergone revolutionary improvements in their design and performance over the last century. The crankshaft is one of the most important components in the engine, which requires regular servicing because it is heavily used. However, repairing the crankshaft via conventional processes is hindered by several factors, including the high cost. Figure 7.19 shows a marine diesel crankshaft repaired using the L-DED process, and good interfacial bonding between the deposited layer and the base metal can be observed. The piston of a four-stroke marine diesel engine is another critical component that can be successfully repaired using L-DED. However, the surface of the piston is prone to damage caused by the high level of forces and temperatures it is subjected to, resulting in the wear of the edges of its grooves. The Kimi Company has not only repaired such pistons by L-DED but also improved the resistance of their grooves against erosion and corrosion.

7.8 Challenges and Risks

Metal powder-based AM has exhibited great potential for applications in the aerospace, biomedical, automotive, molding and tooling, energy, jewelry, and oil and gas industries. It is a cost-effective and time-efficient approach to producing low-volume customized products with complicated geometries and advanced properties. LPBF, L-DED, and EBM are the main processes adopted by the above industries due to their ability to produce dense components with excellent mechanical properties. However, further research and development are still required in terms of design, materials, novel processes and machines, process modeling, and quality control to broaden the range of applications of metal powder-based AM and elevate it to the relatively mainstream technology.

The critical technical challenges of powder-based AM must be overcome through efforts in the research and development of process control, surface finishing, types of heat treatment for the printed components, scalability, processing speed, sustainability, supply chain management and logistics, and qualification and certification.

In particular, the precision and reliability of feedback control systems and predefined metrics must be improved to increase throughput while ensuring consistent quality of the products. Meanwhile, researchers are striving to attain micro- or nano-scale levels of accuracy for refining the surfaces of the printed parts, and the processing speed, energy consumption, water usage, and waste production of AM procedures are expected to be comparable to those of conventional processes for large-volume production. Regarding qualification and certification, the focus should be on material choices, processes, testing, post-processing, and applications. Additionally, an array of business- and market-level challenges exist, such as ethical considerations (e.g. printing firearms), intellectual property/privacy issues, regulatory uncertainties in different countries, limited choices of materials, development of standards, and restrictions of small production runs and scalability.

The risks or uncertainties regarding metal powder-based AM are identified as follows. Intellectual property issues are a primary concern surrounding AM. The ease of access to AM product designs, hardware, and printing materials amplifies the extent of distribution of AM products at the expense of their original creators, particularly through the Internet. Specifically, original digital designs of AM products are difficult to protect through copyright laws, and dealing with the improper usage of such files can be legally challenging, considering that the scope of protection extended to a given work may vary in different countries. Legal issues can also arise when an AM product is manufactured by substandard, incorrectly calibrated, or defective AM equipment or when an original design includes inherent safety hazards. Presently, the development of AM continues to outpace the legal policies pertaining to their usage, thereby introducing uncertainties in terms of user responsibilities and corporate legal obligations. Finally, uncertainties regarding the environmental hazards, toxicity, and chemical degradation associated with the variety of novel print materials introduced for AM still exist, and additional studies are required to determine their long-term effects on humans and the environment.

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